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EMISSIONS SCAVENGING BY FOG, DEW, AND FOLIAGE: FOLIAGE UPTAKE AND CONSEQUENCES FOR PLANTS

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Laboratory and field experiments were conducted to test the hypothesis that acidic emissions from space shuttle launches at Vandenberg AFB, or exposure to ambient acid wet deposition, could deplete foliar nutrients in nearby vegetation. The pH of ambient wet deposition in Indianapolis declined in the order dew > rain > fog. Fog was most effective, and dew least effective, in scavenging chemicals from the atmosphere. However, preexisting leaf surface aerosol contamination, and chemical exchanges between leaf tissues and surface moisture, had a substantial effect on rain and dew chemistry following deposition. These effects, which included increased pH and increased or decreased ion concentrations, were most pronounced for dew because it formed as pure water. Exposure to ambient rains and dews did not measurably influence leaf tissue element concentrations.

Simulated acid mists were applied to several crop species in the laboratory. All species slightly affected leaf surface droplet acidity. Droplets on pinto bean leaves were enriched in potassium, calcium, and magnesium. Tomatoes were raised hydroponically at three different levels of nutrient availability, under conditions where aerosol deposition was minimal. Efflux of ions into whole-plant leachates was observed

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and did not change with time during pH 4.0 and 5.6 mistings. At pH 2.5, efflux of several ions increased dramatically over time, and the rate of increase was positively related to foliage element concentrations. Measurable depletion of foliar nutrients occurred only after single exposures to pH 1.0 mists or after several days of repeated misting at pH 2.5. (A W)

Space shuttle emissions, being extremely acid, have a strong potential to deplete nearby vegetation of nutrients. However, less acid ambient wet deposition also causes nutrient losses. Plants growing on fertile soils may lose ions to acid surface moisture at faster rates than plants growing on impoverished soils. Whole-plant nutrient loss/uptake mass balance studies over the course of repeated exposures to acid wet deposition are needed to determine if these losses are large compared to internal tissue element pools.

B

EMISSIONS SCAVENGING BY FOG, DEW, AND FOLIAGE:

FOLIAGE UPTAKE AND CONSEQUENCES FOR PLANTS

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INTRODUCTION

Chemical emissions during space shuttle launches produce large quantities of hydrogen chloride (HCl) gas, water vapor, and aluminum oxide particles. Condensing water forms exhaust clouds which rise to altitudes of several kilometers and produce highly acidic wet and dry fallout over areas of several square kilometers. At Kennedy Space Center in Florida, the site of all shuttle launches since the inception of the shuttle program, the greatest amount of acid fallout has occurred when convective rainstorms rapidly washed out most of the in-cloud HCl, depositing it in massive, short-term doses to underlying vegetation and soils. Following each shuttle launch, visually apparent foliar damage has been observed within the zone of acid fallout.

In 1984, anticipating a substantial increase in the frequency of shuttle takeoffs, the U.S. Air Force (USAF) and the National Aeronautics and Space Administration decided to launch shuttles from an additional site: Vandenberg Air Force Base on the southern California coast. Vandenberg has a much drier climate than Kennedy, and HCl scavenging from shuttle exhaust clouds there is likely to occur through entrainment in fog droplets or as deposition into dew on leaf surfaces, since fog and dew along that part of the California coast occur more than 15 days per month (Coulombe and Cooper 1975). The scientific literature shows that fogs and dews can be more acid than ambient precipitation and can have higher concentrations of potentially phytotoxic substances. Thus, the potential exists for fogs or dews and shuttle launches to coincide and produce severe impacts on the native vegetation at or around the base.

This three-year research project examined the atmospheric, chemical, and biological processes that determine the potential for such impacts to occur. Due to the cancellation of all shuttle launches after the Challenger explosion, we could not study direct effects of launches on vegetation at Vandenberg AFB. Instead, our efforts were directed to intensive experiments to measure the chemistry of various forms of ambient wet and dry deposition in the Midwest, and to examine in detail chemical interactions between acid deposition and plant foliage. This work included laboratory studies of the effects of simulated mists acidified with sulfuric/nitric acids or HCl on foliar nutrient leaching and foliar chemistry of several crop species.

Our report is organized into two major sections, plus introductory and concluding remarks. The first major section, "Background," reviews the knowledge existing when the study began. The second major section, "Accomplishments," describes in detail a series of field and laboratory studies undertaken during the last 15 months of the project, and reviews the results of earlier experiments described in our first two annual reports (Muir et al. 1986a, 1987). An earlier published paper is included as an Appendix.

HYPOTHESES AND OBJECTIVES

This study focused on an array of hypotheses linking shuttle launch emissions to the chemistry of fog and dew, and to the effects of such emissions on plant foliage. The principal hypothesis being evaluated was:

> Acid fogs and dews on leaf surfaces alter internal leaf chemistry, the effect being mediated in part by ion fluxes across leaf surfaces.

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The subhypotheses relating to the entire linkage from emissions to effects on plants included the following:

(1) Fog water scavenges and, upon subsequent re-evaporation, concentrates chemicals in shuttle launch exhausts onto leaf surfaces.

(2) The ionic composition of liquid on leaf surfaces (resulting from rain, fog, or dew), and of throughfall beneath plant canopies, differs significantly from that of rain and fog droplets because it is modified by interactions with atmospheric chemicals dry-deposited on leaf surfaces, chemicals leached from leaf interiors, and foliar uptake of chemicals solubilized by water on leaf surfaces.

(3) Internal foliar chemistry can be modified by the presence of acidic moisture on leaf surfaces. The extent of this modification depends on rates of ion leaching and uptake.

(4) Plant species differ in the degree of foliar leaching and uptake, and the magnitude of changes in internal leaf chemistry in response to these chemical fluxes.

The original proposal listed a series of objectives outlining the data collection and methods required to test the above hypotheses. These objectives were:

(1) To analyze the chemistry of fog droplets using study sites in the Midwest and at Vandenberg Air Force Base.

(2) To develop methods for analyzing the chemistry of water on foliar surfaces and to relate that chemistry to the chemistry of atmospheric deposition (wet and dry) and to foliar nutrient status.

(3) To examine the effects of acidic fogs and dews on foliar ion leaching and uptake and on foliar chemistry of selected plant species in the Midwest and at Vandenberg AFB, in both the field and laboratory.

Because of the indefinite cancellation of shuttle launches following the Challenger tragedy, Holcomb Research Institute and the AFOSR agreed that the objectives would be modified to focus on the question of the chemistry of acid deposition in general and its effects on plant chemistry. Measurements at Vandenberg AFB were discontinued. The new objectives were:

(1) To measure the chemistry of ambient precipitation and fog in Indianapolis, Indiana.

(2) To measure the chemistry of rain- and dew-derived moisture, and dry-deposited aerosols, on the foliar surfaces of several plant species in Indianapolis.

(3) To explore the relationships between acidic surface moisture and leaf ion leaching/uptake and internal leaf chemistry, as modified by surface aerosols and inherent species' characteristics, in field and laboratory studies in Indianapolis.

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BACKGROUND

The following three subsections review the knowledge base that existed about the time these studies began, and which the HRI research group has utilized in its research.

DIRECT EFFECTS OF SHUTTLE LAUNCHES

Launch Emissions Characteristics

The solid rocket fuel used in space shuttle booster rockets is a mixture of ammonium perchlorate, aluminum, and PBAN. During a normal shuttle burn, fuel combustion produces, by weight, gaseous HCl (17%), particulate aluminum oxide (24%), water vapor (23%), carbon dioxide (33 %), nitric oxide (1%), and iron chloride (<1%), while the shuttle main engines exhaust primarily water vapor (NASA 1978). Total shuttle emissions average 5.4×10^{-2} kg HCl, 7.9×10^{-2} kg aluminum oxide, 2.7×10^{-3} kg nitric oxide, 900 kg carbon monoxide, and 180 kg chlorine gas (Potter 1978). These products, along with steam from injected cooling water and entrained ground debris, form a ground cloud that rises under the influence of buoyancy forces for 4 to 10 min, then stabilizes beneath the local inversion layer at a height of approximately 1 km (NASA 1978).

In-cloud HCl exists in both the gaseous and particulate phases, and decreases exponentially in concentration from near 10 ppm a few minutes following launch to less than 1 ppm an hour later (Pellett et al. 1983). The concentration of aqueous HCl in cloud droplets ranges from 1.9 to 3.6 eq L^{-1}, while HCl aerosol concentrations range from 20 to 125 mg m^{-3} (Pellet et al. 1983). Dry/liquid particle rainout beneath clouds commences within 15 min after launch and contains large-diameter aerosols (80-220 μm) consisting primarily of HCl-acidified water droplets and HCl-coated aluminum oxide particles (Anderson and Keller 1983, Cofer et al. 1983, Sebacher et al. 1984). Total HCl concentrations at ground level range from more than 20 ppm at the launch pad just after launch to less than 1 ppm 0.5 km downwind 90 min later (Swoboda 1983). If the cloud passes beneath convective storms, highly acid (pH 1.0 to 1.5) rain is produced over an area as large as 7 km^2 (Pellett et al. 1983).

Effects on Vegetation

Launch Observations. Shuttle launches at Kennedy Space Center caused mortality or stunted growth of several native plant species close to the launch pad (Knott et al. 1983). The area severely impacted ranged from 5.5 to 9.1 ha. Further downwind, spotting was apparent on the leaves of a number of species. After four launches, plant species composition had changed dramatically near the launch pad, native vegetation giving way to weedy species. Soil concentrations of Al, Cd, Cr, and Mn (all toxic to plants) immediately adjacent to the pad increased significantly after three shuttle launches.

Effects of Aqueous HCl. Mists acidified with HCl, when sprayed on pinto beans, zinnias, and citrus seedlings, caused foliar injury on all species at pH less than 1.0 (Granett and Taylor 1981b). The percent of leaf area affected was 100% at pH less than 0.2. Biomass reductions occurred at pH less than 1.6. In

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some species, plant age affected sensitivity to acid mists; time of day did not effect sensitivity of any species. Repeated acid misting increased the extent of leaf damage (Granett and Taylor 1981b).

Aqueous HCl also affects plant growth. Heck et al. (1962) found that 1000 ppm HCl completely inhibited seed germination, while Lerman (1976) reported 75% inhibition of root growth of crop plants grown in 200 ppm HCl. When 60 mL of HCl solution at pH 0.5 or 1.0 was applied as single large doses to pots containing seeds of plants native to Vandenberg AFB, seedling survival was zero after 30 days (Zammitt and Zedler 1988). For pH 2.5, survivorship was reduced significantly compared to pH 5.6 in most of the species and soil types examined.

CHEMISTRY OF AMBIENT WET DEPOSITION AND AEROSOLS

Chemistry of Rain

pH. Ambient precipitation over much of North America is acidic (pH < 7.0). Water in equilibrium with atmospheric CO_2 has a pH of 5.65, but measurements of precipitation in regions remote from industrial emissions and lacking calcareous dust reveal pH values of 5.0 to 5.6, attributable to small amounts of strong and weak acids (Schindler 1988). Thus, true "acid" rain has a pH below 5.0.

Some recent analyses of precipitation chemistry are shown in Table 1. pH varies from 4.0 to 5.2 across North America (Munger and Eisenreich 1983). The median pH from NADP sites (1979-84) ranged from 4.2 in Pennsylvania to 5.9 in remote areas of the western United States (Knapp et al. 1988). Selected sites in the northeastern U.S. showed pH of 4.1 to 4.4 (Galloway et al. 1987). Ontario precipitation had a pH of 4.2 to 4.4 (Chan et al. 1987).

Ionic Composition. Sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-) are the dominant anions in acid rain (Table 1). The molar ratio SO_4^{2-} to NO_3^- is generally around 2.0-2.5 in rural areas, while NO_3^- may exceed SO_4^{2-} in urban areas. Sulfate and nitrate are derived from absorption of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and nitric acid (HNO_3) gases and from scavenging of aerosols like ammonium sulfate. Chloride (Cl^-) is derived mostly from sea spray, road salt, and fertilizers. Near point sources, HCl gas absorption may also supply Cl^-.

The dominant cation in rain is usually ammonium (NH_4^+) derived from aerosols and, near point sources, ammonia (gas) absorption (Table 1). Calcium (Ca^{2+}) is usually second-most abundant, followed by potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+), all derived from aerosols. A number of heavy metals (Pb, Ni, Zn, etc.) are also found in rain.

In some areas, particularly in cities and industrial regions, absorption of aldehydes - organic weak acids-produces organic anions such as formate (HCO_2^-), acetate ($H_3C_2O_2^-$), and oxalate ($C_2O_2^-$) in rain (Chapman et al. 1986, Kawamura and Kaplan 1986, Gaffney et al. 1987). Many other organic substances occur in rain in trace amounts (e.g., Eisenreich et al. 1981, Gaffney et al. 1987).

Table 1. Observed ranges of pH and ion concentrations in precipitation in North America.

Location	pH	NH$_4^+$	K$^+$	Ion Concentration (μeq L^{-1})						Authors
				Ca^{2+}	Mg^{2+}	SO$_4^{2-}$	NO$_3^-$	Cl$^-$		
North America	4.0-5.2	<10-40	1-10	<10-100	<10-60	<10-60	10-100	<10-50		Munger & Eisenreich 1983
United States	4.2-6.0	0-28		2-27		8-77	2-39			Knapp et al. 1987
Eastern U.S.	4.1-4.4	11-22		3-15		42-73	20-35			Galloway et al. 1987
Ontario	4.2-4.4	13-30		8-22	2-6	30-71	22-46			Chan et al. 1987

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Chemistry of Fog

Radiation fogs occur when the temperature of a layer of air at ground level falls below the dewpoint. This happens either under clear skies and calm winds or when cold air moves across warm water and vice-versa.

_pH_. Reported pH of individual fogs ranges from 2.3 to 7.6, with most values less than 4.0 (Table 2). The range in pH is much greater than for precipitation, reflecting the fact that fog forms locally and scavenges local pollutants, whereas rain may reflect regional scavenging as frontal systems and thunderstorms travel hundreds of kilometers. Fogs can also be an order of magnitude more acidic than individual rainfalls. The most acid fogs occur in highly polluted areas such as Los Angeles (Table 2). When measured at the same location, fog droplets are almost always more acid than rain (Mrose 1966, Waldman et al. 1982, Brewer et al. 1983, Muir et al. 1986b). The reasons for these observations are that (1) fog forms near the ground where pollution is concentrated, (2) fog droplets coalesce around preexisting aerosols, and (3) fog droplets are much smaller than rain droplets, and so dilute pollutants less than does rain (Hileman 1983).

Ionic Composition. Fog droplets often contain substantially greater concentrations of most inorganic ions, and a greater range of variation in ion concentrations among individual fogs, than is the case for rain (compare Tables 1 and 2). Organic substances such as pesticides are much more concentrated in fogs than in rains (Glotfelty et al. 1987).

Chemistry of Dew and Frost

Dew and frost form when the temperature of the collecting surface falls below the dewpoint of the air during calm, clear nights. If this temperature is above freezing, the condensate is dew; otherwise it is frost. Knowledge of dew chemistry remains fragmentary despite 10 years of published speculation that it could be an important input of acidity to vegetation (Brimblecombe 1978, Wisniewski 1982, Chameides 1987). A summary of existing data is shown in Table 3. All of these data are for "bulk dew," i.e., samples collected at the end of individual dew events.

_pH_. Dew pH is highly variable, ranging from 3.6 to 8.5 on chemically inert glass, Teflon, and plastic surfaces, and from 5 to 7 on plant surfaces. No data on the acidity of frosts have been published, although Anderson (1978) indicated that frost pH was similar to dew pH (5.0-6.2) in Maryland. Hoarfrost formed during winter fogs in Utah had pH of 3.9-4.5 (Cerling and Alexander 1987).

Ionic Composition. Chemical composition of dews is quite variable among geographic locations. No single ion is consistently the dominant cation or dominant anion across all samples. The major sources of acidity are SO_4^{2-} and, to a lesser extent, NO_3^-. Nitrite (NO_2^-) is often present in dew, and S(IV) species have also been reported. Therefore, complete oxidation of aqueous sulfur and nitrogen species does not occur in

Table 2. Observed ranges of pH and ion concentrations of fog droplets.

Location	pH	Ion Concentration (µeq L⁻¹)								Author(s)
		NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	NO_3^-	Cl^-	
Bakersfield, CA		490-13300	2-368	7-3500	1-430	1-325	194-9400	200-6800	1-980	Jacob et al. 1984
New England Coast	3.5-7.4						62-2600		0-5780	Houghton 1955
Hamburg, Germany	2.8-4.0									Winkler 1984
Albany, NY	4.3-6.4	70-425	6-290	65-350	6-47	10-101	21-1360	11-218	18-176	Fuzzi et al. 1984
Po valley, Italy	3.5-4.3	560-1620	10-30	60-130	10-50	10-110	400-990	290-1100	20-120	Fuzzi et al. 1985
San Joaquin Valley, CA	2.7-7.2	480-3270		17-169	2-33	6-42	265-2070	250-819	15-122	Jacob et al. 1986
Los Angeles, CA	2.7-7.1	420-4250	8-220	0-230	11-165	30-617	177-938	581-2980	68-423	Brewer et al. 1983
Delhi, India	6.4-7.6	67-427	105-575	314-1417	197-518	313-1087	58-150	26-339	118-307	Khemani et al. 1987
San Joaquin Valley, CA	5.4-6.8	1186-5566				35-118	139-1103	271-1903	17-48	Miller et al. 1987
California coast	2.7-6.2	43-2860	2-148	3-450	4-1500	10-6060	54-2080	6-7900	19-5490	Jacob et al. 1985
Los Angeles area, CA	2.3-5.8	370-10520	4-500	19-2050	17-1380	12-2180	62-5060	130-12000	56-1110	Waldman et al. 1982

Table 3. Mean pH and ion concentration of dews collected from various surfaces.

Surface	pH	Ion Concentration µeq L⁻¹											Location	Author(s)
		NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	SO_3^{2-}	NO_3^-	NO_2^-	Cl^-	HCO_3^-		
Glass	7.3		1	65	11	10	17				6	13	Jerusalem, Israel	Yaalon & Ganor 1968
Glass wool	5.6												Maryland	Anderson 1978
Teflon[1]	4.7			261			139		62		38		Warren, MI	Cadle & Groblicki 1983
Teflon	6.5	65	4	690	31	20	242		166		106		" "	Mulawa et al. 1986
Teflon[1]	5.3	140	19	155	26	37	112	50	52		52		" "	" "
Teflon	4.8	125					78		89	14	84	3	Claremont, CA	Pierson et al., unpubl.
Teflon	4.0	8					81	8	32	1	5		Allegheny Mtn., PA	Pierson et al. 1986
Teflon	6.8	36	9	150	33		32	<1	25	4	6		Indianapolis, IN	This study
Grass	5.5												Maryland	Anderson 1978
Grass	6.0		316			196							Norwich, England	Brimblecombe & Todd 1977
Grass							212						"	Brimblecombe 1978
Maple leaves	6.5	39	252	1285	275	26	676	1	304	0	152		Indianapolis, IN	This study

[1]Generated artificially by cooling.

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dew. Several of the ions commonly present in dew on artificial surfaces (K^+, Ca^{2+}, Mg^{2+}, Na^+) have no possible gaseous sources, suggesting an important role for aerosol deposition in determining dew chemistry.

Chemistry of Aerosols

Overall Chemistry. The atmosphere contains many weak and strong acids that can condense to form aerosols or be adsorbed to the surfaces of pre-existing aerosols. In addition, pollutant gases such as SO_2 and NO_2 can be adsorbed on aerosol surfaces, where they undergo oxidation to produce sulfuric and nitric acids. Hydrogen ion concentrations as large as 5.5 mg m^{-3} have been reported in ambient aerosols (Tanner et al. 1981).

Aerosol SO_4^{2-} concentrations range from less than 1 mg m^{-3} in remote areas to more than 80 mg m^{-3} in highly polluted air, while NO_3^- concentrations vary from less than 1 mg m^{-3} in remote regions to greater than 25 mg m^{-3} in polluted air (Stevens et al. 1980, Alkezweeny and Busness 1984, Dzubay and Stevens 1984. Most aerosol SO_4^{2-} is present in the form of ammonium sulfate, but sometimes substantial concentrations of sulfuric acid may exist (Stevens et al. 1980).

Besides acids, a number of other chemical constituents occur as aerosols. Alkali metals (Ca, Mg, K, Na) are present in the atmosphere as soil and fertilizer dust and sea spray, primarily as salts (e.g., NaCl) and carbonates (e.g., $CaCO_3$). Heavy metals (Pb, Zn, Ni, Cd, Cr, Al, Fe) occur primarily as constituents of soil dust and particles emitted by fossil fuel combustion. Organic carbon (soot) is derived from both fossil fuel burning and natural fires. A wide variety of organic compounds is found in aerosol form (Eisenreich et al. 1981, Gaffney et al. 1987).

Chemistry of Size Classes. Aerosol size distributions are generally bimodal, with one peak of mostly small (0.1-2.0 μm diameter) aerosols, and a second peak of large (> 2 μm diameter) aerosols (Chamberlain 1975). Small aerosols are deposited to surfaces primarily by diffusion through laminar boundary layers and by inertial impaction when the windspeeds are sufficiently large. Large aerosols are deposited both by inertial impaction (when the wind is blowing) and by gravitational sedimentation (during both calm and windy conditions) (Fowler 1980).

The dominant chemical species among small aerosols are ammonium sulfate, heavy metals, and organic/inorganic carbon. For large aerosols, the dominant species are minerals (silicates, carbonates, alkali salts). Some species, such as K^+ and ammonium nitrate, occur in similar relative amounts in both size classes (Hidy et al. 1975, Garland 1978, Whitby 1978, Stevens et al. 1980, Dzubay and Stevens 1984).

EFFECTS OF ACID DEPOSITION ON FOLIAR NUTRIENTS

This review emphasizes the direct effects of acid deposition on foliar nutrient leaching and uptake and internal leaf chemistry. Many other direct and indirect effects of acid deposition have been documented or postulated, including visual injury, reduced or increased growth, altered gas exchange, and soil toxicity

(see review by Evans 1982).

Nutrient Leaching and Uptake

A variety of agricultural plants and forest tree seedlings have been exposed to artificially acidified wet deposition under laboratory conditions. Although the majority of studies have dealt with simulated rain, recent attention has been directed to simulated fogs. Except for a few studies using HCl, all of these experiments used combinations of sulfuric and nitric acids to achieve the desired experimental pH.

Ion Efflux/Influx. We have known for a long time that chemical substances move from leaf interiors to moisture present on leaf surfaces (Tukey 1970). This process is known as foliar efflux or "leaching." Proof that the origin of leached substances includes interior leaf elements was provided by experiments where plants were raised in hydroponic solutions containing radioactively-labeled ions. After plants were subject to distilled water mists, the "leachates" were found to contain the labeled ions (Tukey et al. 1958, Mecklenburg et al. 1966, Evans et al. 1985).

Evidence from recent investigations suggests that acidic wet deposition may enhance foliar ion efflux compared to normal (pH 5.6) rain. For example, efflux rates of K+, Ca^{2+}, Mg^{2+}, NO_3^-, and other ions from foliage of plants grown in controlled environments and exposed to simulated acid rains and mists are often negatively correlated with the pH of the applied solutions (Fairfax and Lepp 1975, Wood and Bormann 1975, Scherbatskoy and Klein 1983). However, Haines et al. (1985a) found no pH dependence for leaching rates of major inorganic cations and anions and Kelly and Strickland (1986) found pH-dependent leaching only for Ca^{2+}.

Foliar influx or "uptake" of ions from surface wetness has been demonstrated experimentally for radioactively labeled sulfur species, Cl, Zn, and Ni (Biddulph et al. 1956, Puckett et al. 1973, Hocking and Hocking 1977, Garsed and Mochrie 1980, Evans et al. 1985).

Foliar ion efflux and influx are also apparent at the branch and whole-canopy level. Compared to ambient rain, throughfall in forests during rain or cloud immersion is usually enriched in K^+, Ca^{2+}, and Mg^{2+}, depleted of NH_4^+ and SO_4^{2-}, and either enriched or depleted of NO_3^- (e.g., Miller and Miller 1980, Cronan and Reiners 1983, Lovett et al. 1985, Olson et al. 1985, Kelly and Strickland 1986, Waldman and Hoffman 1988).

Neutralization of Acidity. Foliar influx of H^+ has been inferred from observations of increasing pH of leaf surface wetness over time. The extent to which this occurs is referred to as "neutralization" or "buffering" of acid surface moisture. A number of laboratory studies have investigated this phenomenon (Adams and Hutchinson 1984, 1987, Craker and Bernstein 1984, Pylipec and Redmann 1984, Evans et al. 1985, Hutchinson et al. 1986). Neutralizing ability is of greatest importance once wet deposition stops and leaf surface water droplets evaporate, concentrating dissolved ions and hence producing a drop in pH (Frevert and Klemm 1984, Unsworth 1984). Factors influencing this ability include species, plant age, and the

temporal pattern of droplet application.

Mechanisms of Ion Efflux/Influx. The physical and chemical mechanisms of leaf ion influx/efflux are poorly understood, especially as much of the observed efflux may be apparent rather than real. Unless leaves are grown in filtered air, their surfaces are always contaminated prior to the onset of wet deposition events by sedimenting and impacting aerosols and by chemicals left on their surfaces by evaporation of preceding wet deposition. The physical presence of these aerosols is revealed by scanning electron microscopy of leaf surfaces (Beauford et al. 1977, Fortmann and Johnson 1984) and by "retention" on leaf surfaces of radioactively labeled ions in applied mists (Anspaugh 1977).

Aerosol "wash-off" is probably the major source of most ions observed in throughfall in the field and is also a confounding influence in many laboratory studies. Time-course studies of the chemistry of individual throughfall events in forests show that most cation and anion enrichment occurs shortly after rain starts, indicating wash-off of surface deposits (Olson et al. 1985). The same pattern appears when individual canopy elements are sprayed with deionized water (Fortmann and Johnson 1984, Reiners and Olson 1984, Lindberg and Lovett 1985).

Plants growing in salty soils exude salts onto their dry surfaces from specialized glands (Salisbury and Ross 1978). Plants are known to release particles directly to the atmosphere, including Pb and Zn (Beauford et al. 1977). Mecklenburg et al. (1966) found no difference in ^{45}Ca efflux from apple leaves into distilled water mists between plants misted in the dark vs. in the light, or mists with and without a respiration inhibitor. Since excretion requires energy, the Ca efflux was not an active process. Reiners et al. (1986), working with balsam fir, demonstrated that most surface chemical contamination was derived from aerosol deposition rather than foliar exudation.

Even when aerosol deposition and leaf exudation are prevented (e.g., by growing plants in filtered air; Hutchinson and Adams 1987) or removed (e.g., by prerinsing leaves prior to applying simulated rain or fog; Scherbatskoy and Klein 1985), there are several potential mechanisms that may explain observed rates of ion influx and efflux. First, mass water flow across the cuticle could occur in response to water potential gradients, perhaps through protein-filled pores. Cuticular permeabilities to liquid water are low (Lendzian 1985), but simulated acid rains and fogs have been observed to erode epicuticular waxes, decrease wax production, and reduce cuticular membrane thickness (Baker and Hunt 1981, Bytnerowicz et al. 1986, Percy and Baker 1987). At these points of damage, mass flow of water, carrying ions with it, could occur. Second, ions may diffuse through cuticular water channels into the underlying apoplast, following concentration gradients. Third, ion exchange— H^+ for base cations — at exchange sites in the cuticle or the underlying apoplast could occur, accounting both for foliar ion efflux and surface moisture neutralization. Finally, active uptake may occur. Foliar uptake of radioactively labeled ions increases in the light and decreases in the presence of metabolic inhibitors (Jyung and Wittwer 1964).

Over the course of eight days, Mecklenburg et al. (1966) allowed a different set of bean plants to absorb ^{45}Ca from nutrient solutions on each day. All plants were were exposed to distilled water mists on

the eighth day. The less time elapsed since ^{45}Ca uptake occurred, the more ^{45}Ca appeared in the leachates, suggesting that Ca was initially "available" for foliar efflux, but later was "immobilized" by deposition in cell walls. The authors then compared the specific activity of ^{45}Ca in several leaf fractions during the course of a 24-hr misting while plants were simultaneously absorbing ^{45}Ca from solution. The changes in specific activity in leachates closely followed changes in exchangeable Ca within the leaves, but not cell sap or non-exchangeable (cell wall) Ca. These results supported the hypothesis of ion diffusion.

Yamada et al. (1964) demonstrated that isolated cuticles were permeable to radioactively labeled Ca^{2+}, Rb, SO_4^{2+}, and Cl, with the rates of ion penetration directly related to surface ion binding. McFarlane and Berry (1974) measured rates of penetration of water and cations through isolated apricot cuticles. Cuticular permeability to ions increased with increasing pH, but pH had no effect on water permeability. Cation permeabilities decreased in the same order as the lyotrophic series for cation exchange in soils. These results suggested that ion penetration of cuticles was by diffusion, but that diffusion rates were altered by ion exchange along the diffusional pathway.

Blanpied (1979) misted apple seedlings with water of pH 3.3 or 4.2, and 0.4 or 1.4 mg L^{-1} Ca^{2+}, for 7 hr. In early summer, neither pH nor Ca^{2+} concentration affected foliar Ca concentrations. In early autumn, at similar Ca concentrations in control leaves to those in early summer, low pH/low Ca^{2+} mists significantly reduced foliar Ca, while high pH/high Ca^{2+} mists significantly increased it. Leaf K concentrations were reduced in all treatments, regardless of mist pH or Ca^{2+} concentration. These results suggest that both ion exchange (enhanced at low pH) and diffusion (Ca efflux at 0.4 mg L^{-1} Ca^{2+}, Ca influx at 1.4 mg L^{-1} Ca^{2+}) mechanisms caused changes in leaf Ca concentrations.

Contrary to Blanpied's (1979) findings, Hutchinson and Adams (1987) found no influence of differing foliar Ca concentrations on neutralization of acid droplets applied to surfaces of beet and sunflower leaves, implying that Ca^{2+}, at least, was not involved in ion exchange reactions.

Foliar Chemistry

Net efflux and influx of ions may lead to nutrient deficiencies and excesses, respectively, in leaf tissue. In fact, leaching of cations from foliage is one proposed explanation for the current forest decline symptoms in Europe and North America (e.g., McLaughlin 1985, Schutt and Cowling 1985). Yet surprisingly little experimental work has been directed toward the influence of acid rain and fog on changes in internal foliar nutrient status.

Blanpied (1979) reported reduced K and Ca concentrations in apple leaves subject to simulated rain of pH 3.3 or 4.2. Hindawi et al. (1980) found that foliar concentrations of N, Ca, Mg, and P decreased as pH of simulated acid rain decreased, but K concentrations were unaffected. Pinto beans grown in pH 3.0 nutrient solutions were depleted of Ca and enriched in Mg compared to plants grown in pH 5.0 solutions (Trites and Bidwell 1987). However, Kelly and Strickland (1986) found no change in leaf nutrient concentrations of tulip poplar and white oak plants treated repeatedly with simulated acid mists in soil-plant microcosms.

Summary

Visual injury and mortality of plants resulting from extremely acid (pH < 1.5) wet deposition has been observed following shuttle launches. Such low pH values do not occur in ambient wet deposition. Reported pH ranges from 4.0 to 6.0 in precipitation, 2.3 to 7.6 in fog, and 3.6 to 8.5 in dew. Minimum pH values below which visual damage occurs to plants exposed to acidic rains and fogs range from 1.5 to 3.5 (Haines et al. 1980, Granett and Musselman 1984, Jacobson 1984, Jacobson et al. 1987, Musselman 1988, Musselman and Sterrett 1988). Thus, among the various forms of wet deposition, only fog has the potential to cause visual injury.

However, even "pure" wet deposition of pH 5.6 may remove elements in ionic form from foliage by the mechanisms of ion exchange or diffusion. From laboratory misting experiments, ions such as K^+ and Mg^{2+} are known to be enriched in throughfall or in leachates, while others, in particular NH_4^+, are depleted. In field studies, and in many laboratory experiments, wash-off of previously deposited aerosols from leaf surfaces may account for much of the observed ion enrichment. Nevertheless, the often-observed negative correlation between pH and ion enrichment, and the ability of leaf surfaces to partially neutralize acid solutions on their surfaces, suggest that (1) ion efflux and influx do occur between leaf interiors and surface moisture, and that (2) the lower the pH of incident wet deposition, the greater the flux rates of ions out of leaves. Thus, the potential exists for acid wet deposition to deplete foliar nutrients.

There is a strong need for experiments that (1) measure the response of foliar element concentrations to exposure to acidic solutions, (2) directly examine leaf ion efflux and influx in the absence of previously deposited aerosols, and (3) quantitatively assess the potential for ion efflux into acid solutions to deplete foliar nutrient pools.

APPROACH AND ACCOMPLISHMENTS

INTRODUCTION

Our overall objectives were twofold: (1) to measure fluxes of chemical species to vegetation in rain, fog, and dew in the field in Indianapolis, and (2) to study the interactions between acidic wet deposition and plant foliar chemistry in the field and under controlled laboratory conditions.

In fulfillment of the first goal, we have (1) measured the volume and ion concentrations of ambient precipitation; (2) measured the ion concentrations of several fogs; (3) measured the volumes and ion concentrations of dew formed on Teflon and leaves; and (4) estimated aerosol deposition rates to foliage.

To attain the second goal, we have (1) tested the ability of two plant species to neutralize acid droplets on their leaf surfaces in the field and in the laboratory; (2) examined interactions between leaf chemistry, aerosol deposition, and dew deposition in the field; (3) examined the influence of pH and source of acidity on droplet neutralization and foliar chemistry in the laboratory; and (4) studied the influence of pH and plant nutritional status on whole-plant ion fluxes between acidic mists and foliage in the laboratory.

In the following subsections, we describe objectives, methods, results, and interpretation separately for each of our experiments. Only brief summaries are presented for experiments previously described in detail in the 1985-86 and 1986-87 annual reports (Muir et al. 1986a, 1987) and in a publication (Muir et al. 1986b). More detail is provided for experiments conducted in 1987-88. We conclude with a general discussion of our findings.

STUDY SITE

Our field work for these studies was conducted at the Butler University Environmental Preserve (BUEP) on the floodplain of the White River in Indianapolis (elevation 160 m). The experiments were carried out inside a fenced area (15 x 50 m) located near the edge of a large open field. The BUEP is part of the Butler University campus, located in northwest Indianapolis, a large (population 675,000) urban center. Numerous local and regional emission sources for a variety of gaseous and particulate air pollutants surround the site, including coal-burning power plants, chemical and fertilizer industries, heavy vehicular traffic, and intensive agriculture. Rainfall has been acidic (pH < 5.0) for decades throughout Indiana, and Indianapolis has for many years failed each summer to meet federal air quality standards for ozone, carbon monoxide, and sulfur dioxide. These facts suggested that the acidity of wet and dry deposition in Indianapolis would be high and that the chemistry of rain, fogs, dews, and aerosols would be complex and varied. Thus, the BUEP was an excellent site for acid deposition and foliar effects research.

Treatment of experimental plants with simulated acidic wet deposition took place in laboratories at Holcomb Research Institute (HRI) and Butler University. Plants were grown in the Butler University greenhouse or in controlled-environment chambers maintained by HRI and the Butler University Biology Department.

CHEMICAL ANALYSES

Our research entailed extensive analysis of anions and cations in water and foliage samples at HRI's analytical laboratory. Therefore, attention was directed early in the project to developing good quality assurance procedures for chemical analyses. The results of these investigations are described in detail in Muir et al. (1986b, Appendix A).

Aqueous samples were filtered (if necessary) and stored at $4^{\circ}C$ in darkness, with 0.2% chloroform added to retard microbial growth, until chemical analyses could be conducted. pH was measured with an Orion-Ross model 810300 electrode connected to a Fisher Accumet model 640A pH meter. Specific conductances were measured with a Sybron-Barnstead model PC-70CB conductivity bridge.

Anions (SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, Cl^-, HCO_3^-, and organics) and ammonium (NH_4^+) were measured with a Dionex model 2010 ion chromatograph with a conductivity detector. The analytical columns employed micromembrane suppression. Sample analysis was automated and included software chromatogram peak analysis using a Hewlett-Packard series 9000, Model 216 microcomputer. Metal cation (K^+, Ca^{2+}, Mg^{2+}, Na^+) analyses were performed on a Perkin-Elmer model 305B atomic absorption spectrophotometer, using flame vaporization.

Foliar samples were oven dried for 48 hr at $50^{\circ}C$ and stored in paper bags. Prior to analysis, they were ground in a Cyclotec model 1093 sample mill to pass a 0.4-mm mesh, dry-ashed at $450^{\circ}C$ for 4 hr in porcelain crucibles in a muffle furnace, dissolved in nitric acid, and diluted to the desired volume with distilled, deionized water. These samples were then analyzed for cation concentrations, using atomic absorption spectrophotometry.

Our water analysis methodologies were tested against certified water samples provided by the U.S. Environmental Protection Agency and the National Bureau of Standards (NBS). NBS tomato leaf samples were used to test the analyses of foliar samples. The standard deviation of percent ion recovery was always less than 0.6% for water samples and 1.5% for foliar samples.

All samples were analyzed in duplicate. Ion balance [(Σcations - Σanions)/(Σcations + Σanions) x 100] and conductivity (sum of individual ion specific conductances at $25^{\circ}C$ and infinite dilution) were calculated for each aqueous sample. If ion balance differed more than 15% from unity, or if the ratio of measured conductivity differed by more than 20% from calculated conductivity, the sample was reanalyzed.

CHEMISTRY OF AMBIENT WET DEPOSITION
IN INDIANAPOLIS

Rain and snow, and to a lesser extent fogs and clouds, are the best documented and best understood of the aqueous atmospheric scavenging media. However, it is still unclear whether or not a chemical signature representing local pollutants in urban areas, or at industrial facilities and major military bases, appears in local wet deposition. The effectiveness of dew, the most "local" of all forms of wet deposition, as a scavenging medium is poorly known. Because of these gaps in our knowledge, we compared the chemistry of rains, fogs, and dews at our study site.

Chemistry of Rain

Methods. Since July 1985, wet and dry deposition samples have been collected at the BUEP and the samples analyzed according to protocols of the National Atmospheric Deposition Program (NADP 1984). This involved sampling of cumulative weekly precipitation using an Aerochem Metrics wet/dry deposition sampler. Rain accumulated in plastic buckets which were exposed to the atmosphere only during rain events. Precipitation amounts were measured separately with a Belfort recording rain gauge. Rain samples were analyzed for pH, conductivity, and ion concentrations. Sampling has continued for a three-year period, commencing in July 1985. Data from calendar year 1986 are representative of the entire period, and are described below.

Results and Discussion. Volume-weighted ion concentrations were lower than simple concentrations because of dilution by more intense and longer lasting rains (Table 4). There were narrow ranges between maximum and minimum values for all chemical parameters. For example, pH ranged from a low of 3.77 to a high of 5.13, with a weighted mean of 4.30. Annual mean pH was remarkably constant over the three-year period, varying by only 0.01 pH unit. Rainfall was almost always more acidic than the 5.65 expected from chemical equilibrium with atmospheric CO_2.

Data are used for December 1985 through November 1986, to allow a comparison of seasons as defined by NADP (winter = December-February, spring = March-May, summer = June-August, fall = September-November). Monthly weighted mean pH reached a minimum value in the hottest, driest month, August, and a maximum value in September (Fig. 1). In general, the most acidic rainfall occurred in summer, and the second most acidic in winter. Since sulfuric and nitric acids are primarily responsble for rain acidity, maximum SO_4^{2-} concentrations in summer probably accounted for the low summer pH, while maximum NO_3^- concentrations in winter accounted for the low winter pH (Fig. 1).

A positive correlation existed between pH and precipitation amount (Fig. 1). Presumably, the majority of acidic species in the atmosphere are scavenged by falling raindrops early in rainfall events, so that additional rainfall diluted the acidic species deposited in the sampling bucket until the next collection was made.

Ammonium and calcium showed maximum values in early spring, coinciding with intensive spring plowing of surrounding agricultural lands (Fig. 2) Presumably, plowing generated dust from the calcaerous soils typical of most of Indiana and from carbonate fertilizers; these dusts were subsequently scavenged by falling rain. Maximum values of Na^+ and Cl^- occurred in winter and were tightly correlated (Fig. 2). This result suggests that dust from road salt, used extensively during snow and ice storms in Indianapolis, was being scavenged by local rain.

A comparison between our sampling site and the rural NADP stations in Indiana is illuminating (Table 5). The station directly west of Indianapolis, in Bondville, IL, reported an annual weighted mean pH that was 0.03 pH units higher than Indianapolis. In contrast to this result, the Delaware, OH, station directly east of Indianapolis reported an annual weighted mean pH that was 0.05 pH units lower than Indianapolis.

Table 4. Chemistry of rainfall sampled in Indianapolis between 01-7-86 and 12-30-86[a].

Ion	Mean	Weighted Mean[b]	Maximum	Concentration $(\mu eq\ L^{-1})$
F^-	1.8	1.3	14.1	0.0
Cl^-	5.4	4.1	20.8	1.1
NO_3^-	33.2	22.7	120.5	6.7
$H_2PO_4^-$	2.6	1.8	13.8	0.0
SO_4^{2-}	68.7	59.3	181.4	23.9
Na^+	3.3	2.9	17.4	0.3
K^+	1.2	0.9	4.6	0.0
NH_4^+	23.1	17.0	62.5	0.0
Ca^{2+}	17.8	11.9	84.2	1.6
Mg^{2+}	3.9	2.9	13.2	0.0
H^+	63.8	54.2	169.8	7.4
Ion Balance (%)[c]	-0.88	-0.85	8.43	-12.05
Measured pH	4.25	4.30	5.13	3.77
Calc/Meas pH[d]	1.00	1.00	1.10	0.96
Conductivity % Difference[e]	0.09	-0.32	6.26	-15.48

[a]Data shown are from 44 valid samples. Of the 52 sampling periods, eight yielded insufficient sample size for complete analysis. None were rejected for failing one or more of the three quality control tests.

[b]By volume of precipitation

[c]$[(\Sigma cations - \Sigma anions)/(\Sigma cations + \Sigma anions)] \times 100$

[d]Calculated $[H^+] = \Sigma cations - \Sigma anions$ (except H^+) $+ HCO_3^-$; however, HCO_3^- proved to be negligible in all cases.

[e]$[(Calculated\ cond. - measured\ cond.)/(measured\ cond.)] \times 100$. Calculated conductance = sum of the individual ion conductances at infinite dilution at 25°C.
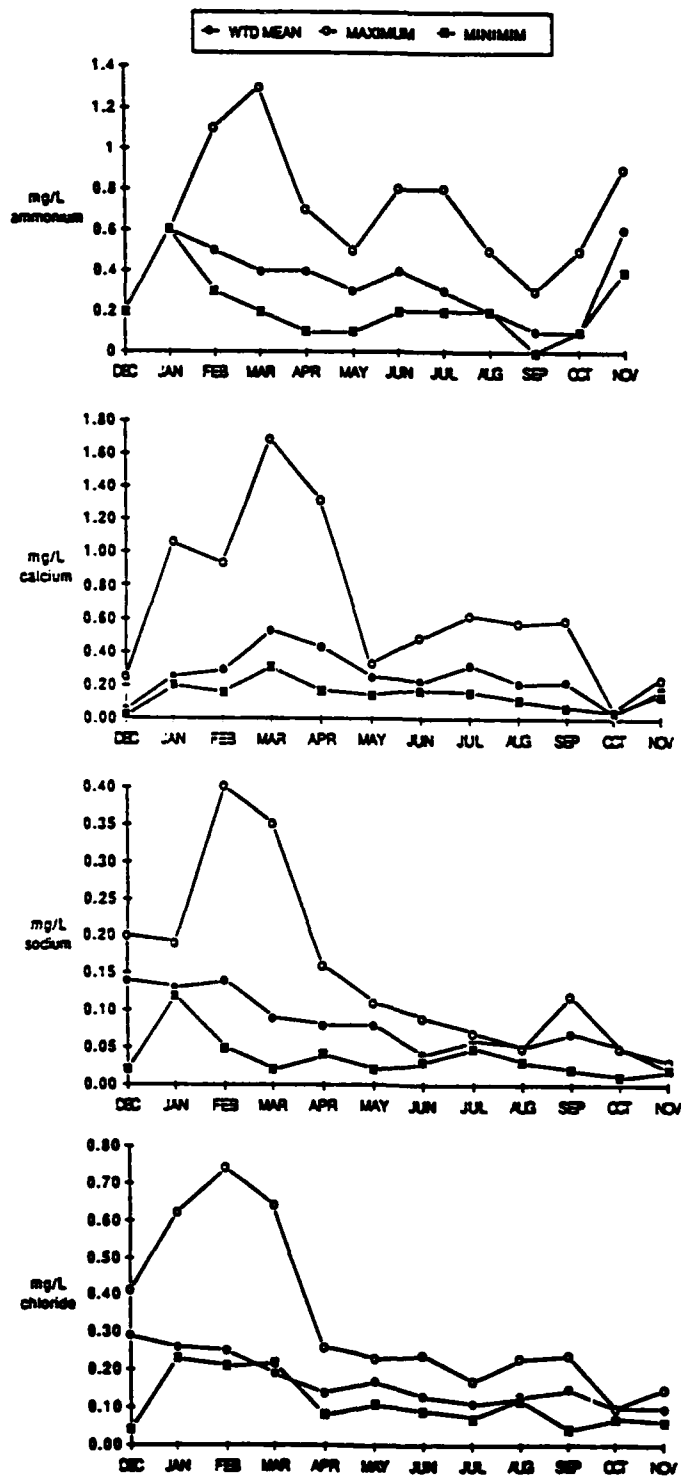
Figure 2. Monthly mean, maximum, and minimum ammonium, calcium, sodium, and chloride concentrations in weekly rainfall samples collected in Indianapolis.
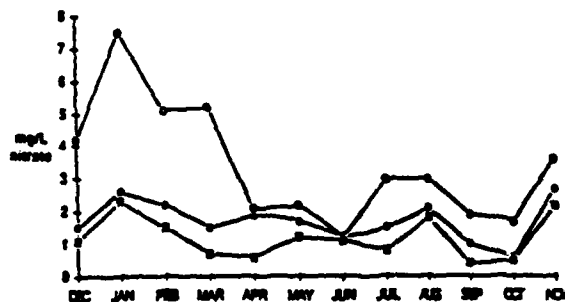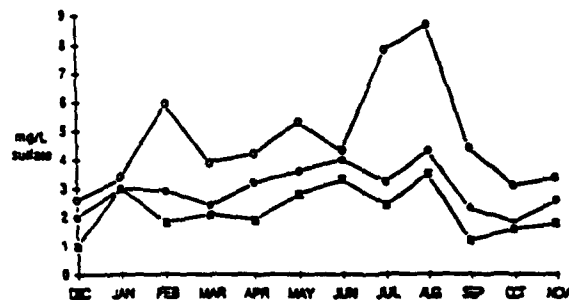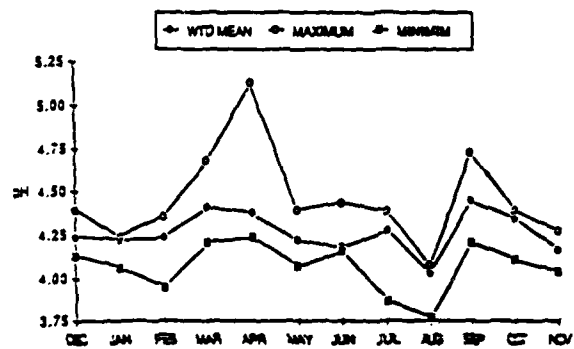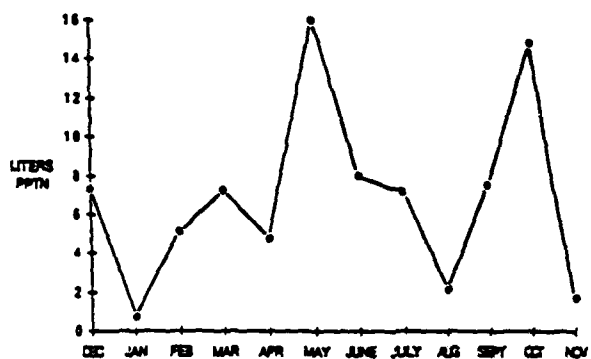
Figure 1. Monthly precipitation, and monthly mean, maximum, and minimum pH and sulfate/nitrate concentrations in weekly rainfall samples collected in Indianapolis.

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Table 5. Comparison of pH and ion concentrations (mg L^{-1}) in rainfall sampled in Indianapolis and surrounding NADP sampling sites between 01-7-86 and 12-30-86.

Ion	BU[a]	IL[b]	OH[c]	ID[d]	HR[e]	PU[f]	SW[g]
Cl$^-$	0.15	0.13	0.12	0.15	0.12	0.13	0.27
NO$_3^-$	1.41	1.29	1.69	1.44	1.84	1.69	1.23
SO$_4^{2-}$	2.85	2.69	3.00	2.78	3.25	3.21	2.77
Na$^+$	0.068	0.056	0.061	0.074	0.056	0.066	0.140
K$^+$	0.037	0.018	0.016	0.026	0.026	0.025	0.079
NH$_4^+$	0.31	0.25	0.29	0.29	0.42	0.48	0.21
Ca^{2+}	0.24	0.17	0.16	0.31	0.26	0.24	0.25
Mg^{2+}	0.035	0.024	0.032	0.057	0.052	0.041	0.039
pH	4.30	4.33	4.25	4.41	4.32	4.33	4.47

[a]Butler University Environmental Preserve, Indianapolis, IN
[b]Bondville, IL
[c]Delaware, OH
[d]Indiana Dunes, IN
[e]Huntington Reservoir, IN
[f]Purdue University, IN
[g]Southwest Purdue Agricultural Center, IN

This is consistent with the general decrease in pH values going from east to west in the United States, particularly from the Ohio Basin eastward (NADP 1987). The annual pH and ion concentrations from Indianapolis rainfall were in excellent agreement with those shown on NADP annual isopleth maps for 1986 (NADP 1987), from which it can be inferred that there is no obvious influence of the urban location of the Indianapolis sampling site relative to the rural NADP sites. Yet, Indianapolis annual mean pH was lower than the average of the four NADP sites operating in Indiana (Table 5). Determining whether or not this represents an urban effect will require several years of similar comparisons.

As was the case at all surrounding NADP stations, rainfall acidity in Indianapolis was generated primarily by sulfuric and nitric acids, present in a mass ratio of about 2:1 (Table 5). Even though the pH in Indianapolis was lower than all sites except Delaware, OH, the annual weighted mean SO_4^{2-} concentration in Indianapolis was third highest, and NO_3^- concentraton was fourth lowest, among the sites in Table 5. This result suggested a relative paucity of neutralizing species in the Indianapolis atmosphere compared to the other sites. In fact, NH_4^+ and Ca_2+ concentrations were both fourth lowest among the sites. Thus, despite lower SO_4^{2-} and NO_3^- concentrations than several other sites, pH remained comparatively low in the absence of sufficient neutralizing species. It appeared that the lower pH in Indianapolis was less of an urban effect, i.e., enhanced levels of acidic species due to higher burning of fossil fuels, than it was a dimunition of a rural effect, i.e., neutralization of acidic species by carbonate dusts and agriculturally generated ammonia.

Chemistry of Fogs

Methods. We sampled the chemistry of six fog events during the winter of 1985-86. Detailed methods and results were presented in a publication (Muir et al. 1986b; see Appendix to this Final Report). A summary of those measurements is provided here. We used two types of collectors: a Cal-Tech rotating arm collector (Jacob et al. 1984) and a Cal-Tech active strand collector (Jacob et al. 1985a). The samplers were located on open, level ground inside the fenced area of the BUEP. Rotating-arm samples were collected for six fog events. Sampling time was 20 to 190 min, commencing at dawn and ending before the fog dissipated. Strand collections occurred over three successive, 85-min time periods starting at 0800 hr during a single February fog.

Results and Discussion. The fogs were consistently quite acid (pH < 4.1), with the lowest measured pH at 2.85 (Table 6). Sulfate and nitrate were the dominant anions in all samples, but the SO_4^{2-} to NO_3^- ratio varied from 0.78 to 2.56. These differences may reflect a varying ratio of atmospheric SO_2 gas and SO_4^{2-} aerosols to atmospheric NO_x ($NO+NO_2$) gases and NO_3^- aerosols. Phosphate was the third most important anion.

Ammonium was the major cation (Table 6), with fertilizer dust and gaseous NH_3 emissions from the agricutural lands surrounding Indianapolis as probable sources. Similarly, Ca^{2+} and Mg^{2+} in the fog samples were probably derived mostly from agricultural fertilizer calcareous soil dusts. The Na^+ and Cl^-

Table 6. Ion concentrations and pH in fogwater collected at the Butler University Environmental Preserve. At the observed pH, PO_4^{3-} is a mixture of HPO_4^{2-} and $H_2PO_4^-$. Ion balance is (Σcations-Σanions)/(Σcations+Σanions) x 100 (μeq L^{-1}).

Date	Volume (mL)	pH	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	NO_3	Cl^-	PO_4^{3-}
					Rotating Arm Collector						
11-25-85	10	3.33									
12-09-85	16	3.10	676	11	100	37	26	731	943	68	165
12-10-85	8	3.17									
01-23-86	10	3.76	1300	19	808	226	108	1240	1000	140	727
02-02-86	3	2.85									
02-18-86	30	4.03	671	4	25	8	17	604	236	114	180
02-18-86	11	3.92	743	7	35	14	30	391	353	114	121
					Screen Collector						
02-18-86	85	4.06	820	4	35	7	27	672	284	143	217
02-18-86	75	3.78	787	5	31	3	32	589	344	185	222
02-18-86		3.74	721	5	35	8	33	454	371	142	160

ions, and some of the Ca^{2+} ions, may have come from the road salt used extensively in Indianapolis during the winter. Ion balances were within ±10% of unity.

Fog pH was lower, and most ion concentrations higher, than in rain sampled at the same site (compare Tables 4 and 6). This result may reflect several processes: (1) lower volume of water in fog compared to rain droplets, (2) coalescence of fog droplets around local aerosols, and (3) a greater influence of local pollutants on fog than on rain. Much of the water in rain originates from distant locations, so that rain chemistry tends to reflect upwind regional atmospheric chemistry. This supposition was supported by the very similar chemical characteristics of rain in Indianapolis and surrounding stations (Table 5). Fog droplets, on the other hand, form locally and scavenge local pollutants. Because urban areas generally have higher concentrations of pollutant gases (SO_2, NO_2, HNO_3, etc.) and acidic aerosols, one would expect lower pH and higher concentrations of many ions in fogs compared to rains.

Chemistry of Dews and Frosts

Methods. Regular monitoring of dew and frost chemistry commenced in June 1987. For routine dew measurements, we used an artificial collector consisting of 0.50-μm-thick Teflon attached to a 3-cm-thick polystyrene block by double-stick tape. The polystyrene insulated the Teflon, encouraging dew formation. The collector was hinged in the middle. When a dew was expected due to suitable weather conditions (clear, calm nights), the collector was thoroughly rinsed with distilled, deionized water, dried, folded over, and taped shut to prevent contamination of the Teflon (analysis of the final rinsewater revealed no cations or anions above analytical detection limits). At sunset, the collector was placed on top of a 1-m-high table in the BUEP and opened.

Dew collection occurred the following morning at dawn. Because Teflon is hydrophobic, dew formed small (< 1 mm diameter) droplets on the collector. These were swept together with a chemically clean Teflon scraper, sucked up with a pipette, and transferred to clean polyethylene bottles.

From mid-autumn 1987 until mid-spring 1988, frosts formed instead of dews. These were scraped off the collector into a chemically clean plastic container, melted at room temperature, and the water transferred to sample bottles. A total of 20 dews, 12 frosts, and 2 "slushes" was sampled. The slushes, which occurred in spring, consisted of liquid water in the collector center and frost around the edges.

The chemical composition of dew droplets on real leaf surfaces was observed on two occasions. At dawn on two mornings in August 1986, individual dew drops were removed from sugar maple and dogwood leaf surfaces, using a pipette, and transferred to clean plastic bottles. To obtain sufficient volume for chemical analysis, droplets were composited within species. At dawn on eight mornings in August and September, 1987, dew was removed from sugar maple leaves by shaking 10-20 saplings over a chemically clean plastic container. These collections were concurrent with dew collections from the Teflon collector. All dew samples were filtered and analyzed for pH, cations (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+), and anions (SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}).

During summer 1988, three dew events were intensively studied to examine overnight changes in dew chemistry and their relationship to atmospheric concentrations of pollutant gases (SO_2, NO_x, O_3, and NH_3) and aerosols. Multiple Teflon collectors of the design previously described were used. Collectors were deployed as previously discussed, but at specified time intervals after the start of dew formation (usually every 2 hr), all of the dew was removed from a portion of one collector. Three to four samples were collected nightly, each containing all of the dew formed on part of a collector from the start of dew formation to the time of sampling.

Two dews were sampled in this manner at the BUEP. Ammonia was drawn across an oxalic acid-impregnated filter by a portable, battery-powered pump. Air containing ozone was drawn by a pump through a small impinger containing potassium iodide solution. The iodine liberated in the absorbing solution was determined spectrophotometrically. Air containing SO_2 was drawn through a separate impinger containing formaldehyde. The SO_2-formaldehyde adduct was measured by ion chromatography. Mean gas concentrations were calculated at 2- to 4-hr intervals from filter/solutiuon ion concentrations, filter surface areas/solution volumes, pump flow rates, and duration of sampling. The impingers were deployed on top of the table at the BUEP, adjacent to the Teflon collector.

An additional dew was sampled at a different site in southwest Indianapolis: an open field about 40 m from an ambient air quality monitoring station run by the Indianapolis Air Pollution Control Division (IAPCD). This site was adjacent to a pharmaceutical company manufacturing plant and about 3 km downwind from a large, coal-burning power plant. Collectors and impingers were deployed at ground level. Hourly averages of SO_2, NO_2, and O_3 concentrations at a height of 5 m were provided by the IAPCD.

Results and Discussion. Of all forms of wet deposition—rain, fog, clouds, dew—the chemistry of dews should most clearly reflect local atmospheric chemistry. No scavenging by sedimenting droplets occurs, so only those pollutants in the air immediately above dew-forming surfaces are likely to be deposited to dews.

Individual dews and frosts varied in pH from slightly acidic to slightly alkaline (Table 7). Ion concentrations were extremely variable among individual dews. Bicarbonate was always more concentrated than was SO_4^{2-}, and Ca^{2+} was always more concentrated than NH_4^+, in both dews and frosts. Nitrite (NO_2^-) occurred in all dews and frosts, and sulfite (SO_3^{2-}) was observed in about one-third of the samples. The organic anions formate (HCO_2^-) and acetate ($H_3C_2O_2^-$) were often present ($\leq$ 12 meq L^{-1}) in both dews and frosts. Ion balances were generally negative, indicating the presence of other, unmeasured anions (Table 7). Dews, frosts, and slushes did not differ significantly in pH or ion concentrations (Fig. 3).

Dew on maple leaves was slightly more acidic than dew and frost on Teflon (Table 8, Fig. 3). Concentrations of all ions except NH4+ were significantly higher (t-tests, P < .05) in maple leaf dews than in simultaneously-occurring Teflon dews and frosts (Fig. 3). Preexisting leaf surface aerosol contamination, or ion efflux out of leaves into dews, probably accounted for these differences. On the two days sampled in 1986, dogwood leaves caused greater neutralization of dew, and had higher concentrations of all ions in dew droplets on their surfaces, than did maple leaves (Table 8).

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Table 7. Ion concentrations and pH of dews collected from a chemically-inert teflon collector in Indianapolis, 1987/-88. At the observed pH, PO_4^{3-} is a mixture of HPO_4^{2-} and $H_2PO_4^-$, and very little CO_3^{2-} is present. HCO_2^- is formate and $H_3C_2O_2^-$ is acetate. Ion balance is (Σcations − Σanions)/(Σcations + Σanions) × 100, in μeq L^{-1}.

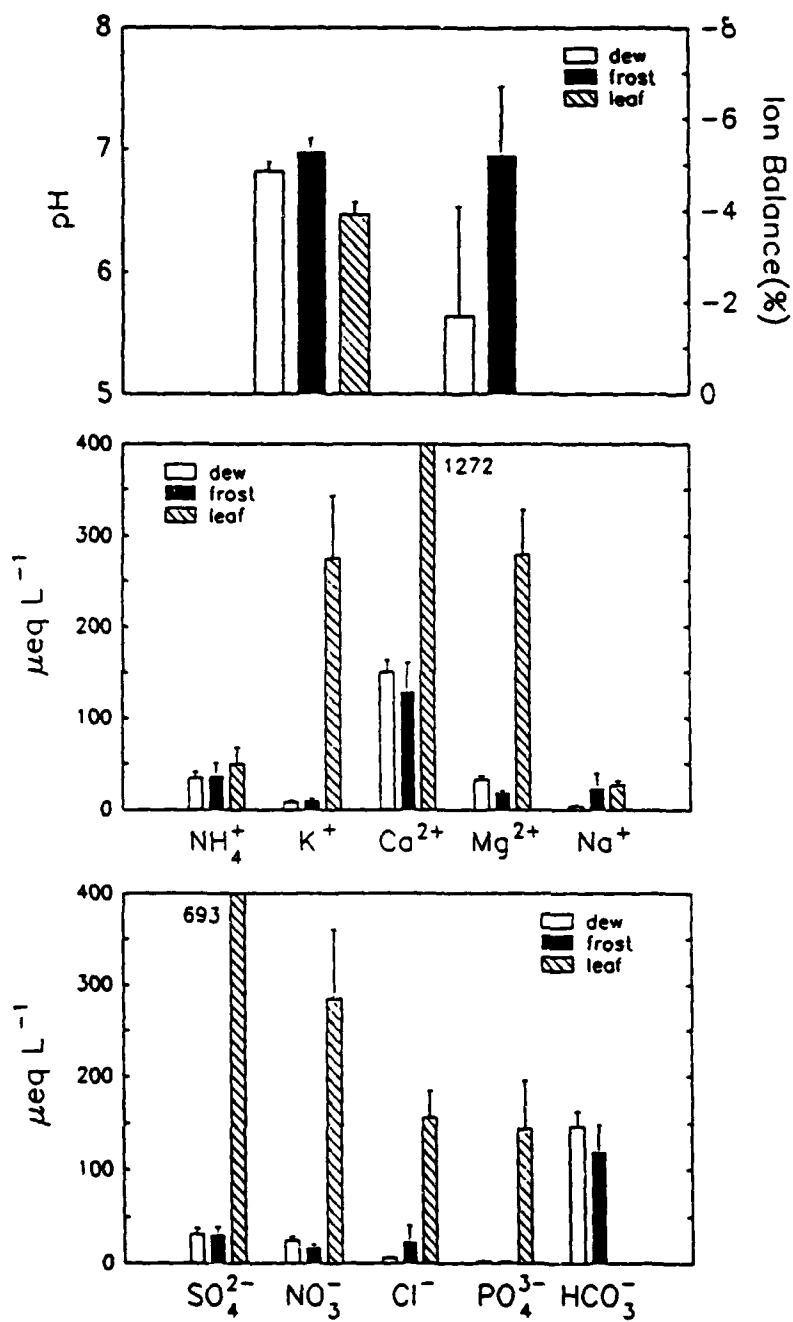| | Volume | | | | | | | Ion Concentration (μeq L^{-1}) | | | | | | | | | | Ion bal- |
Date	(mL)	pH	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	SO_3^{2-}	NO_3^-	NO_2^-	Cl^-	PO_4^{3-}	HCO_3^-	HCO_2^-	$H_3C_2O_2^-$	F^-	ance (%)
								Teflon collector dews										
06-10	126	6.32	4	4	142	69	3	6	0	8	1	4	0	163	0	0	8	-7
06-17	109	6.18	15	5	92	51	3	9	0	21	3	4	0	116	2	0	3	-3
06-18	81	6.44	78	8	121	60	4	54	2	45	2	6	2	136	12	0	10	0
06-25	104	6.72	33	5	122	63	2	11	0	15	2	4	1	210	0	0	7	5
07-15	139	6.72	12	6	73	25	6	4	0	2	1	6	0	152	2	0	0	15
07-17	125	6.89	13	4	78	20	4	8	0	8	2	4	1	146	2	0	3	19
07-21	176	7.30	30	9	266	22	4	40	0	22	3	6	4	374	8	0	6	17
07-23	128	7.32	101	7	182	15	3	84	0	55	3	7	2	169	5	0	7	4
07-24	114	7.34	105	11	153	18	9	106	0	36	3	12	2	177	5	0	6	8
08-07	103	7.06	27	5	109	52	2	17	0	27	2	3	2	121	2	0	2	-5
08-19	104	7.02	20	6	122	39	5	10	0	20	2	3	2	128	2	0	4	-5
09-03	62	7.26	43	26	253	37	3	31	0	39	5	16	9	193	6	0	1	-9
09-23	167	6.44	9	4	50	17	3	22	0	9	4	5	1	43	0	0	1	-1
09-24	117	6.87	9	16	255	20	1	16	0	15	4	6	3	220	0	0	1	-7
09-25	118	6.45	21	19	183	38	2	34	0	22	2	6	6	172	0	0	3	-4
11-04	127	6.36	16	3	140	12	5	61	2	21	9	4	5	50	3	0	3	-6
04-04	153	6.95	21	12	174	21	5	31	2	16	9	8	2	92	5	0	10	-9
05-17	79	6.84	80	12	164	39	7	52	2	78	5	4	3	69	0	17	8	-14
05-27	148	7.07	24	4	194	13	3	20	2	24	10	7	1	135	0	3	1	-9
06-05	108	6.75	27	7	127	22	4	15	1	25	9	4	1	58	0	0	1	-24
								Teflon collector slushes										
05-02	124	6.33	32	8	52	19	5	14	3	20	9	0	2	13	6	18	7	-13
06-10	54	6.76	19	15	122	30	9	17	0	26	9	13	3	169	1	1	1	10
								Teflon collector frosts										
11-06	98	6.72	15	6	61	13	2	9	0	7	1	6	2	56	4	0	1	-6
11-12	95	7.01	10	4	135	13	3	12	0	13	1	6	1	113	3	0	1	-5
11-19	77	6.66	7	2	45	9	2	15	0	7	0	5	1	31	0	0	3	-4
12-05	139	6.64	3	1	33	12	6	9	0	9	0	7	1	28	0	0	1	-1
12-18	56	7.30	0	7	467	23	203	92	0	41	0	217	1	328	0	0	4	-1
03-10	119	6.82	33	2	118	18	15	27	5	12	2	18	1	86	9	4	3	-6
04-04	128	6.99	18	3	97	17	4	12	1	12	3	0	1	75	4	4	2	-10
04-08	46	7.39	169	26	181	17	14	79	3	24	0	7	8	258	1	1	2	-2
04-13	43	7.48	113	31	131	50	16	62	0	39	2	0	7	241	11	1	12	5
04-19	141	7.38	21	16	121	18	7	24	0	14	4	3	0	116	0	0	3	-6
04-20	112	7.20	31	13	107	16	4	13	1	17	2	0	2	89	0	1	1	-15
04-29	123	6.18	15	4	34	9	3	14	1	10		7	1	7	7	5	1	-11

Figure 3. Chemistry of dews (n = 20) and frosts (n = 12) formed on Teflon, and dews (n = 9) formed on sugar maple leaves in Indianapolis, 1987-88. Values are means with standard error bars. Top panel: pH and ion balance. Middle panel: cation concentrations. Bottom panel: anion concentrations.

Table 8. Ion concentrations and pH in dews collected from petri dishes and sugar maple and dogwood leaves in Indianapolis. At the observed pH, PO_4^{3-} exists as a mixture of HPO_4^{2-} and $H_2PO_4^-$.

| Date | pH | | | | Ion Concentration (μeq L^{-1}) | | | | | |
		NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}
				1986 Collections						
				petri dishes						
08-05	5.59		21	234	79	23	167	74	178	102
08-12	5.61		50	77	15	80	30	11	138	22
				Maple Leaves						
08-05	6.13		29	589	166	6	300	3	147	6
08-12	6.47		50	244	33	19	116	8	163	16
				Dogwood Leaves						
08-05	7.42		335	2535	303	11	929	11	7	35
08-12	7.12		534	1617	81	98	693	16	255	32
				1987 Collections						
				Maple Leaves						
06-17	6.45	12	107	569	132	12	269	242	148	8
06-18	6.59	7	40	185	43	4	128	67	57	7
07-21	6.83	7	56	848	106	16	352	226	32	25
07-23	6.78	6	157	2265	371	34	1024	656	85	56
07-24	6.60	8	178	2196	365	44	864	684	162	225
09-14	6.29	145	432	1382	349	31	939	271	186	427
09-23	5.87	108	532	1507	487	46	1051	137	266	248
09-24	6.51	78	514	1327	346	23	777	146	279	279

During the first overnight dew, most ions showed diminishing concentrations throughout the night, apparently because of dilution as dew formation rates accelerated (Table 9). However, after initial dilution, most ion concentrations remained roughly constant in the second dew. Slower dew formation rates (i.e., less dilution) the second night may have been the primary reason. There was little change in pH either night; it remained nearly neutral (Table 9). We hypothesize that H^+ resulting from dissociation of acids was neutralized by sedimenting carbonate dust, since Ca^{2+} and HCO_3^- were present at substantial concentrations (Table 9).

We calculated ion accumulations by multiplying concentrations by dew volumes. Less SO_4^{2-} and SO_3^{2-} accumulated the first than the second night (Fig. 4), probably due to higher SO_2 concentrations the second night (Table 10). Somewhat more Ca^{2+} and HCO_3^- accumulated the second night than the first night. Interestingly, the much higher NO_2 concentrations the second night (Table 10) did not produce a corresponding increase in dew NO_3^- and NO_2^- accumulation (Fig. 4), possibly because of low deposition velocities for NO_2, a fairly insoluble gas (Lee and Schwartz 1978).

Because winds during dew formation were light (dew won't form if windspeed exceeds 3 m s^{-1}; Monteith 1957), deposition of small aerosols to the Teflon collectors was probably small. However, dry "fallout," the gravitational sedimentation of large aerosols, was probably substantial. Field and wind tunnel measurements of aerosol deposition clearly show much lower deposition velocities for small aerosols than for large aerosols, especially at low windspeeds (Chamberlain 1975, Thorne et al. 1982, Voldner et al. 1986). Cadle and Groblicki (1983) found that, despite similar volumes of water, dew on the top of a horizontal plastic surface collected five times as much Cl$^-$ and nine times as much Ca^{2+} as dew on the bottom surface, a result consistent with dry deposition dominated by fallout.

The presence of ions (K^+, Ca^{2+}, Mg^{2+}, Na^+) that lacked any gaseous sources in the dews formed on Teflon indicated that these ions entered dews as sedimenting aerosols. In addition, dew concentrations of HCO_3^- were much greater than absorption of atmospheric CO_2 could provide (e.g., 12 meq L^{-1} in water at a fixed pH of 6.5 and atmospheric CO_2 = 350 ppm) (Table 5). Thus, the likely source of HCO_3^- was also aerosols, specifically calcareous soil dust and Ca/Mg fertilizer dust. Yaalon and Ganor (1968), Cadle and Groblicki (1983), and Mulawa et al. (1986) similarly concluded that carbonate dust was a major source of dew neutralization. Alkaline aerosols are also known to neutralize acidity in rain (Applin and Jersak 1986, Moller and Zierath 1986) and fog (Khemani et al. 1987).

Our finding of similar SO_4^{2-} and NO_3^- concentrations in dews and frosts (Table 7) suggested that most inputs of these species occurred via aerosol sedimentation rather than absorption and subsequent oxidation of SO_2, NO_2, and HNO_3, since gaseous absorption is minimized to ice.

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Table 9. Temporal chemistry of dews formed on Teflon collectors in Indianapolis, 1988. On the first night, samples were collected at the Butler University Environmental Preserve. On the second night, samples were collected near an Indianapolis Air Pollution Control Division air quality monitoring station. Times and deposition amounts are cumulative from the start of dew deposition. (Volume of dew formed per m² of collector survace area.) pH and ion concentration data the same as in Table 5.

Date	Time (hr)	Deposition (ml m⁻²)	pH	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	SO_3^{2-}	NO_3^-	NO_2^-	Cl^-	PO_4^{3-}	HCO_3^-	HCO_2^-	$H_2C_2O_2^-$	F^-	Ion balance (%)
07-01	2.0	16	6.98	74	39	290	36	12	36	3	3	6	1	11	198	62	50	6	-9
07-01	5.2	50	7.15	42	15	176	29	5	22	2	18	7	9	2	108	26	21	2	-10
07-01	7.7	81	7.43	36	11	177	30	5	19	2	22	8	9	1	117	20	16	2	-9
07-28	2.0	23	7.56	83	7	639	45	10	65	22	59	25	37	3	542	20	10	3	0
07-28	4.0	59	7.41	64	8	465	40	10	48	22	49	30	21	2	325	16	12	2	-5
07-29	6.0	86	7.52	77	5	427	33	17	62	20	47	28	28	2	322	14	11	2	-7
07-28	8.0	119	7.45	62	8	426	29	24	55	19	40	28	24	0	331	13	7	2	-3

Table 10. Pollutant gas concentrations during the dew sampling of Table 9 and Fig. 4. During the first night, concentrations were measured with impingers. Concentrations the second night were measured with continuous analyzers (SO_2, NO_2, O_3) and with an impinger (NH_3). Time is cumulative from the start of dew deposition.

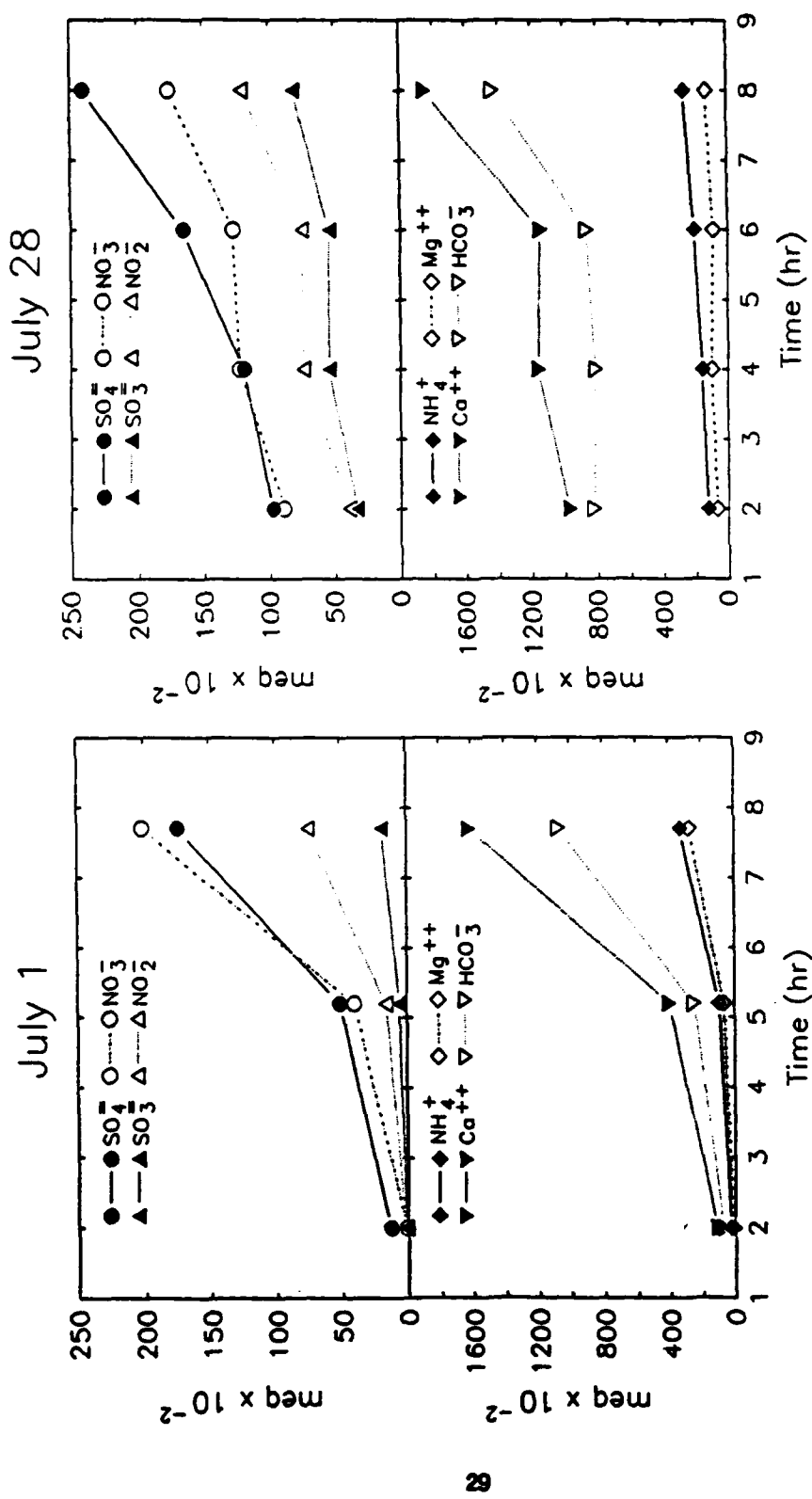| Date	Time (hr)	SO_2	NO_2	O_3	NH_3
07-01	2.0	0	6	24	
	5.2	0	6	17	
	7.7	0	5	18	
07-28	2.0	8	49	12	6
	4.0	6	62	1	6
	6.0	6	63	1	6
	8.0	6	65	1	6

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Figure 4. Temporal changes in the total accumulation of sulfur and nitrogen species (top panel) and cations and bicarbonate (bottom panel) in dews forming on Teflon collectors in Indianapolis in summer 1988.

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ACID DEPOSITION AND FOLIAGE CHEMICAL INTERACTIONS
IN THE FIELD

INTRODUCTION

Our review of the literature (see BACKGROUND) indicates that acidic wet deposition interacts chemically with leaf surfaces, primarily by washing off previously deposited substances and by ion influx and efflux between leaf interiors and leaf surface moisture. Among dozens of laboratory and field studies, only a few have attempted to distinguish between these two processes. There are surprisingly few appropriate data with which to evaluate the hypothesis that acidic wet deposition can influence foliar nutrient status.

With this deficiency in mind, we launched a combined field and laboratory experimental program with the following objectives: (1) to estimate rates of dry deposition of aerosols to foliage in the field; (2) to evaluate the separate influences of solubilization of pre-existing dry deposition and leaf ion influx/efflux on the chemistry of rain and dew on leaf surfaces; (3) to study the rates of ion influx/efflux between leaves and simulated acid mists in the laboratory; and (4) to examine the effects of individual rain and dew events in the field, and simulated acid mist treatments in the laboratory, on internal foliar chemistry. In this section, we describe the field studies.

RAIN, AEROSOL, AND FOLIAGE CHEMICAL INTERACTIONS

Our studies of rain/foliage chemical interactions were intended to (1) evaluate the feasibility of using surrogate collectors in place of leaves for collection of dry and wet deposition; (2) estimate rates of dry deposition to leaf surfaces; (3) measure the ability of leaf surfaces to neutralize acidity in rain droplets; and (4) determine whether or not concentrations of foliar elements were measurably altered by rain events.

Methods

Field Procedures. Sampling procedures are described in detail in Muir et al. (1986a, 1987), but are reviewed briefly here. Both real leaves of *Acer saccharum* (sugar maple) and *Cornus florida* (flowering dogwood), and "surrogate" leaves of man-made materials were employed as collecting surfaces. Three-year-old maple and dogwood saplings were transplanted in 1985 to a 15 x 30 m area of the BUEP which was mowed monthly. Surrogate collectors were of two types: (1) "dry-only"—used to collected sedimenting and impacting aerosols during rainless weather; and (2) "wet-only"—used to collect natural rains. Collectors used in summer 1986 included and Teflon petri dishes used as dry-and wet-only collectors, and small Teflon discs used as dry-only collectors. Chemical analyses of distilled, deionized water rinses of these collectors showed that they were free of chemical contamination. Petri dishes were deployed on wooden posts at 0.5- and 1.2-m heights adjacent to the saplings. The Teflon discs were mounted horizontally on flexible Teflon strips which allowed them to flutter in the breeze, similar to real leaves. In the 1987 field work, only polycarbonate petri dishes at 1.2-m height were used, as deposition in 1986 seldom differed among the alternative collector types, and never differed between heights (see Results).

Previous workers had shown that petri dishes provided estimates of dry deposition that, for many ions, compared favorably with washates from real leaves (Dash 1985, Dolske and Gatz 1985, Lindberg and Lovett 1985, Lovett and Lindberg 1985). Collection efficiencies for some ions, however, were greater or lesser for dishes than for real leaves.

Dry-only collectors were deployed in the field at the start of rainless periods and removed just before the next rain event. Wet-only collectors were deployed and removed at the beginning and end of individual rain events. Because most rains overflowed the wet-only petri dishes, rain volumes. Upon removal, dry-only collectors were placed individually into Ziploc bags free of chemical contamination. Rainwater in the wet-only collectors was poured into plastic bottles.

Foliage was collected from saplings of each species at the beginning of each rainless period, as soon before each rain as possible, and as soon as leaves had dried after each rain. Samples consisted of five pools of leaves from each species, each pool containing 4-8 leaves. Only leaves free of obvious contaminants and tissue damage, were chosen. Each leaf was placed in a Ziploc bag and returned to the laboratory.

During or immediately after a rain, droplets were collected from leaves using plastic syringes and pooled by species in polypropylene sample bottles. We chose to collect droplets rather than throughfall from beneath the sapling canopies because (1) throughfall includes liquid that contacts plant parts other than leaves, i.e., interactions of foliage with rain may be confounded by liquid that ran off branches, and (2) throughfall samples include liquid that does not contact foliage.

Laboratory Procedures. Aliquots of the rain samples from the wet-only collectors were analyzed for pH within 1 hr of collection. On the same day, the dry-only collectors were washed individually by swirling with 40 mL of distilled, deionized water for 5 min, an aliquot was removed for pH measurement, and the remainder of each washate was stored in a plastic bottle at $4^{o}C$.

The petiole of each leaf was coated with paraffin wax. Then the leaf was sealed inside a 500-mL plastic bottle and shaken for 2.5 min with 25 mL of distilled, deionized water to remove surface aerosols. Previous leaf washing studies by Lovett and Lindberg (1985) with chestnut oak leaves indicated that the highest concentrations of ions in leaf washates occurred within the first few minutes, indicative of wash-off of aerosols. Our choice of a 2.5-min wash time was based on leaf washing kinetics studies conducted with four broadleaf species, including sugar maple and dogwood (Muir et al. 1986a, Appendix B). After washing, the leaves were stored at $4^{o}C$ in darkness until chemical analysis.

Rain samples (wet-only collectors, rain droplets on leaves) and washate samples (dry-only collectors and rinsed leaves) were analyzed for cations (NH_4^+, K+, Ca^{2+}, Mg^{2+}, Na^+) and anions (SO_4^{2-}, NO_3^-, Cl$^-$, PO_4^{3-}, F-). Each leaf was analyzed for the elements K, Ca, Mg, and Na. Projected (1-sided) leaf areas were measured with a Numonics model 1224 digital planimeter. Ion concentrations in rain and washate samples were expressed as milliequivalents per square meter (meq m^{-2}; 2-sided surface area for leaves, inside surface area for petri dishes).

Statistical Analyses. Inputs of dry deposition were estimated using two methods: (1) assumed equal to the ion concentrations in washates from dry-only collectors, and (2) by subtracting ion concentrations in leaf washates from the beginning of dry periods with those in washates from foliage collected just prior to rain events. If leaves and surrogate collectors were equally efficient at "capturing" aerosols, and if our leaf-washing procedures efficiently removed surface aerosols without ion efflux from the leaf interiors, these two methods would yield similar results.

Aerosol deposition rates and ion concentrations were compared between surrogate collectors at 0.5 and 1.2 m height, between surrogate collectors and real leaves, and between sugar maple and dogwood leaves, using unpaired t-tests. Comparisons between the three types of surrogate collectors were carried out by analysis of variance (ANOVA) using SPSS software (Hull and Nie 1981). Pearson's correlation was used to investigate relationships between the accumulation of ions on surrogate/natural leaf surfaces and the length of the preceding dry period.

Results

Results have been presented in detail in Muir (1986a) and are reviewed here. Four complete dry weather/rain events were sampled in summer 1986, plus two additional dry periods. The length of the rainless periods varied from 77 to 239 hr, the length of rain events from 3 to 12 hr, and the rain amount from 0.13 to 3.20 cm.

Aerosol Deposition. Aerosol deposition rates ($mg\ m^{-2}\ h^{-1}$) in 1986 did not differ between surrogate collector types deployed at 0.5 and 1.2 m, nor between polycarbonate petri dishes, Teflon petri dishes, and Teflon discs (minimum P from ANOVA or t-tests = .26). Aerosol deposition rates did not differ significantly among polycarbonate petri dishes, maple leaves, and dogwood leaves for Ca^{2+}, Mg^{2+}, SO_4^{2-} or PO_4^{3-} (Table 11). For K+, Na^+, NO_3^- and Cl⁻, aerosol deposition rates were identical to petri dishes and maple leaves and significantly less to dogwood leaves (Table 11).

The total amount ($mg\ m^{-2}$) of aerosols accumulated on polycarbonate petri dishes during dry weather was positively and significantly (P < .05) correlated with the length of the dry period for all ions except PO_4^{3-} and F⁻ (Table 12). In contrast to this result, only 12 out of 19 correlations for ions on leaf surfaces were significant, and only two of the significant correlations (NO_3^- and PO_4^{3-} on maple leaves) were positive; the rest were negative.

Droplet Neutralization. Foliage of both maple and dogwood partially neutralized (increased the pH of) incident rain, with dogwood consistently producing greater neutralization (Table 13). There was no relationship between incident rain pH and the degree of neutralization for either species.

Changes in Foliar Elements. Element concentrations in maple and dogwood foliage at the end of each rain event were either higher or lower than at the start of the event, with no consistent pattern for any ion across

Table II. Estimated rate of accumulation of elements (mg m^{-2} h^{-1}) over dry
intervals on polycarbonate petri dishes and on foliage of dogwood
and maple. Data are mean (± 1 standard error) of average rates for
each of the five dry periods.

Ion	Petri Dish	Dogwood	Maple
Ca^{2+}	21.99 (2.09)	30.04 (12.68)	19.43 (10.66)
Mg^{2+}	4.44 (0.72)	5.37 (1.85)	5.35 (2.78)
Na^+	1.29 (0.32)	0.25 (0.29)	0.15 (0.24)
K^+	4.34 (0.92)	0.18 (1.55)	3.66 (2.93)
Cl^-	2.61 (0.89)	0.79 (0.94	1.38 (1.33)
NO_3^-	17.70 (4.03)	-8.05 (8.59)	9.84 (5.46)
PO_4^{3-}	1.61 (0.32)		3.94 (3.43)
SO_4^{2-}	33.65 (3.24)	24.81 (5.80)	40.31 (18.77)

Table 12. Relationships of quantities of elements accumulated on foliar and artificial surfaces during dry intervals (mg m^{-2}) to the duration of dry exposure in days (Pearson's correlation coefficient, r, and one-tailed probabilities, p). Sample sizes are five dry periods, ranging from 2-10 days. Aritificial collectors were Teflon plates, Teflon discs, and polycarbonate petri dishes.

| | Collector | | | | | |
| | Artificial | | Dogwood leaves | | Maple leaves | |
Ion	r	p	r	p	r	p
Ca^{2+}	.583	.000**	-.401	.023*	-.578	.001**
Mg^{2+}	.494	.000**	.047	.412	-.389	.028*
Na^+	.341	.003**	-.475	.008**	.013	.476
K^+	.513	.000**	-.260	.105	-.732	.000**
F^-	.212	.172	-.669	.017	-.521	.050*
Cl^-	.342	.003**	-.648	.000**	-.459	.010**
NO_3^-	.697	.000**	.753	.001**	-.061	.385
PO_4^{3-}	.148	.126	.525	.009**	-.587	.001
SO_4^{2-}	.623	.000**	-.733	.000**	-.636	.000

* $p \leq .05$
** $p \leq .01$

Table 13. pH of rain collected in petri dishes, and rain droplets collected from leaf surfaces, at the Butler University Environmental Preserve in 1986. Data are means from 3-8 replicate dishes and single values for droplets pooled within each species.

	Time	Collecting Surface		
Date	(hr)*	Dishes	Maple	Dogwood
06-06	10	4.27	4.34	5.55
06-30	2	3.99	4.50	6.25
06-30	5.5	4.30		5.99
06-30	8	4.30	4.04	6.26
07-26	12	3.72	4.87	7.05

*Time elapsed since start of rain

Table 14. The difference in element concentrations in sugar maple and dogwood leaves (mg kg^{-1} dry leaf mass) before and after rain events at the Butler University Environmental Preserve, 1986.

Date	K^+	Ca^{2+}	Mg^{2+}	Na^+
		Sugar Maple		
06-06	-116	+480	-4	+2.5
06-17	+324	+2180	+116	-9.1
06-23	-386	+340	+112	-26.6
06-30	-26	-620	-2261	+0.8
07-26	+468	-2960	-1094	
08-06	+196	-1340	-290	+1.3
		Dogwood		
06-06	-33	+100	-150	-16.2
06-17	+68	-820	-100	+17.0
06-23	+273	+1195	+354	-26.5
06-29	-760	-1420	+14	+2.0
07-261	-25	+1065	+66	-2.9
08-06	+738	-900	-234	

the various rain events (Table 14). None of the before after comparisons were significant (minimum P = .28). There was an upward trend in foliar concentrations of Ca and Mg in maple, and of Ca in dogwood, and a downward trend in foliar concentrations of Mg and K in dogwood, during the summer (Table 14).

Discussion

Aerosol deposition rates were remarkably similar between petri dishes and maple and dogwood leaves (Table 11). The few differences that were observed were probably attributable to variations in leaf orientation and surface roughness and the effectiveness of our rinsing method for removing leaf surface aerosols. Windspeed and aerosol concentration variations with height probably were not important because aerosol accumulation was identical to petri dishes at 0.5 and 1.2 m heights. The negative deposition rate of NO_3^- to dogwood leaves implied that some mechanism existed for NO_3^- flux into the leaves or for its conversion to another chemical form on the leaf surfaces. Deposition rates were also negative for some specific combinations of ion, species, and dry period; these were obscured by the use of means across all dry periods in Table 11. Although no rain occurred during these dry periods, dew probably formed on many of the nights with clear skies. Thus, ion exchange or diffusion could have been operating during dew events as surface aerosols were solubilized, and this might have accounted for the apparent depletion of NO_3^- on dogwood leaves.

If aerosols simply accumulated on leaf surfaces, correlations between total ion deposition and the lengths of the preceding dry periods should always have been positive. In fact, most significant correlations were negative (Table 12). This could have happened if ion fluxes into leaves occurred during dews. However, K^+ and Mg^{2+} consistently show efflux from leaves into throughfall or simulated acid mists (see BACKGROUND). This would increase surface concentrations of these ions, and, hence, make the correlations for these ions strongly positive, whereas they were negative in our experiment (Table 12).

Both species exhibited rain droplet neutralization, with dogwood more effective (Table 13). A possible explanation for this neutralization was ion exchange involving H^+ in droplets displacing K^+, and possibly other cations, from cation exchange sites inside the leaves. Dogwood leaves had significantly greater concentrations of K than did maple leaves (t-test, P > .05; Table 14) and, possibly, had greater K^+ efflux.

The lack of significant differences in foliar element concentrations before and after individual rain events over a two-month period (Table 14) indicated that, individually or cumulatively, ambient rain in Indianapolis, which has a pH as low as 3.8 (Table 14), did not affect the foliar nutrient status of dogwood and sugar maple saplings.

DEW, AEROSOL, AND FOLIAGE CHEMICAL INTERACTIONS

Our studies on dew/foliage chemical interactions were divided into two areas: (1) measuring the chemistry of dew on leaf surfaces, and (2) evaluating the influence of pre-existing dry deposition and ion influx/efflux on the net deposition of ions to leaf surfaces by individual dew events. We use the term net deposition because, unlike the situation with rain, we measured ions remaining on leaf surfaces at the end

of dew events, when all surface moisture had evaporated. Gross chemical deposition in dews could be greater or lesser than net deposition, depending on the influence of solubilized surface aerosols and depletion or enrichment of ions in dew due to leaf ion influx efflux.

Methods

Field Procedures. At 0800 hr on the day before an expected dew event (as anticipated by meteorological conditions), five or seven pairs of chemically clean petri dishes were placed in holders mounted 1.2 m above the ground. One dish in each pair was randomly allocated to a "dry-only" treatment, the other dish to a "bulk" treatment. Seven sugar maple saplings were randomly selected from the population of saplings at the BUEP (n = 50), excluding saplings with excessive insect or drought damage to leaves, or those sampled during a previous dew event.

The twelve largest leaves from each sapling were marked with flagging, avoiding leaves with more than 2% of their area either necrotic or eaten by insects. The marked leaves on each sapling were randomly allocated to three treatments: four to "dry-only," four to "bulk," and four to "wet-only." The dry-only and bulk leaves were rinsed on both surfaces with distilled, deionized water, using hand-held spray bottles.

Twelve hours later, at 2000 hr, the dry-only petri dishes and leaves were removed and placed individually into clean Ziploc bags. Each dry-only petri dish was replaced with a new, chemically clean, "wet-only" petri dish. The wet-only leaves were rinsed as described above, with the bulk leaves temporarily covered with plastic bags to prevent accidental wash-off of chemicals from their surfaces. The following morning, once dew had completely evaporated from the leaves and petri dishes (between 0800 and 0900 hr), the remaining dishes and leaves were placed into separate Ziploc bags.

Exposure times were 12 hr for dry-only samples, 12-13 hr for wet-only samples, and 24-25 hr for bulk samples. The proportion of exposure time for wet-only samples during which dew was present was variable; sometimes dew formation began in late evening, sometimes not until later at night.

Laboratory Procedures. Leaf and petri dish samples were stored at 4°C for 24 hr. Each petri dish was then rinsed by swirling with 40 mL of distilled deionized water for 2 min. The first leaf in each treatment from each sapling was placed into a clean Ziploc bag with the base of the petiole extruding from the bag to avoid contamination by xylem exudates. 40 mL of distilled deionized water were added to the bag, the bag was sealed around the petiole, and the leaf was rinsed for 2 min by gently tilting the bag back and forth. This procedure was repeated for the remaining three leaves in each treatment, using the same 40 mL of water. Washates from petri dishes and leaves were poured into plastic bottles and stored at 4°C.

Samples were analyzed for pH, cations (Na^+, K+, Ca^{2+}, Mg^{2+}, NH_4^+), and anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}). Phosphate analyses were stopped after the first three dew events, as 3/4 of the samples were below analytical detection limits. Concentrations of NO_3^- in several samples were also below detection limits; these values were treated as zeroes in the statistical analyses.

Concentration data (meq L^{-1}) were divided by the corresponding collector surface areas to normalize for differences in surface area among samples. Thus, the units reported here are meq m^{-2}. Surface areas were the sum of the bottom surface and inside rims of the petri dishes (107.8 cm^2) and twice the projected area of the four leaves in each sapling sample (365-832 cm^2), as both leaf surfaces collected dew and dry deposition. The projected (1-sided) areas of leaves were measured with a digital planimeter.

<u>Statistical Analyses</u>. For the dew/foliage chemical interaction experiment, dry deposition of ions in the absence of dew and leaf efflux/influx was represented by the dry-only petri dishes. Dry deposition in the absence of dew but with leaf efflux/influx occurring was represented by the dry-only leaves. Net deposition during dew in the absence of previous dry deposition and leaf efflux/influx was represented by the washates from the wet-only petri dishes. Net deposition during dew in the presence of leaf efflux/influx was represented by the washates from the wet-only leaves. Net chemical deposition during dews in the presence of previous dry deposition was represented by the difference between the washates from the bulk and dry-only petri dishes. Net deposition during dews in the presence of both leaf efflux/influx and previous dry deposition was represented by the difference between the washates from the bulk and dry-only leaves. For calculations of bulk-minus-dry chemical concentrations, bulk and dry-only samples were paired within petri dish holders or individual maple saplings.

Results

Wet-only and dry-only petri dish samples always contained detectable concentrations of each ion (Table 15). For petri dishes, dry-only concentrations were either less than, similar to, or greater than wet-only concentrations, even though exposure times (12 hr) were similar (Table 15).

Because treatments were paired within petri dish holders and saplings, the significance of between-sample variation was assessed using 3-way ANOVA with presence/absence of dry deposition and presence/absence of leaf efflux/influx as main effects and sample number as an unreplicated blocking factor (Sokal and Rohlf 1981, p. 356). Between-sample variation was not statistically significant (P > .05) for any ion on any date. Therefore, the analysis was carried out again as a completely-randomized, two-factor (leaf efflux/influx, dry deposition) ANOVA (Table 16). No clear pattern was evident for any treatment or ion. On individual days, different combinations of treatment effects significantly affected each ion, and the pattern for one day was not repeated on other days. With the exception of July 14, the leaf efflux/influx X dry deposition interaction was significant for at least one ion (Table 16).

Discussion

We knew from the results of the rain/foliage chemical interaction experiment that deposition rates of all ions were similar for petri dishes and maple leaves (Table 11). In this experiment, however, significant differences were frequently found between petri dishes and maple leaves in terms of total amounts of accumulated ions during dry periods (Table 15). There are two possible explanations for this disparity: (1)

Table 15. Concentrations (means ± 1 standard error) of ions in washates from chemically inert (polycarbonate petri dishes) and chemically active (sugar maple leaf) surfaces.

Type of Surface	Treatment	Ion Concentration (ueq m^2)						
		Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
				June 10				
petri dish	wet-only	1.68(0.35)	1.68(0.74)	2.16(0.57)	1.13(0.38)	1.14(0.47)	20.00(0.69)	7.45(0.38)
	dry-only	3.01(0.45)	2.99(0.46)	3.86(1.84)	2.16(0.10)	1.33(0.57)	15.92(1.50)	7.15(0.87)
	bulk minus dry	0.98(0.38)	3.23(0.49)	2.16(2.15)	0.87(0.92)	1.71(0.92)	10.37(2.08)	2.99(1.20)
maple leaf	wet-only	5.71(0.84)	5.35(1.73)	11.37(3.05)	1.76(0.17)	5.77(1.08)	36.42(5.57)	14.89(2.39)
	dry-only	7.01(1.11)	3.50(1.17)	6.48(1.01)	1.59(0.20)	6.29(0.59)	31.83(1.93)	4.56(0.95)
	bulk minus dry	-3.03(1.20)	4.70(2.37)	0.22(1.60)	0.11(0.23)	-1.23(0.42)	5.90(3.40)	0.61(1.79)
				June 18				
petri dish	wet-only	1.32(0.05)	8.14(1.37)	15.61(0.79)	0.87(0.04)	1.90(0.00)	21.11(1.11)	8.12(0.62)
	dry-only	0.63(0.28)	10.89(0.58)	3.55(1.05)	0.81(0.14)	2.09(0.19)	24.81(2.84)	10.87(1.87)
	bulk minus dry	2.15(0.52)	7.03(0.62)	21.44(1.65)	0.73(0.40)	3.56(1.47)	15.28(6.21)	4.73(3.78)
maple leaf	wet-only	11.61(6.10)	11.41(3.05)	40.99(10.49)	6.12(2.13)	7.46(1.20)	52.93(10.60)	19.48(4.57)
	dry-only	4.90(1.03)	10.11(0.85)	11.41(2.39)	5.36(1.20)	5.29(0.82)	31.21(2.77)	12.06(0.83)
	bulk minus dry	1.92(3.65)	0.66(1.23)	4.09(3.07)	-1.27(0.99)	-0.52(0.80)	4.31(4.57)	1.63(1.47)
				July 8				
petri dish	wet-only	1.44(0.11)	5.27(0.12)	19.78(0.80)	1.74(0.09)	3.42(1.52)	81.10(0.69)	7.76(1.19)
	dry-only	0.96(0.34)	2.51(0.35)	4.02(1.33)	0.71(0.15)	10.44(8.87)	15.55(5.51)	5.80(3.00)
	bulk minus dry	2.28(0.89)	5.15(0.45)	23.18(1.22)	1.97(0.30)	2.09(14.93)	15.55(5.48)	3.79(3.29)
maple leaf	wet-only	4.98(0.39)	4.06(0.27)	18.72(1.76)	4.90(0.32)	4.56(0.38)	16.24(1.22)	4.31(0.46)
	dry-only	6.42(1.62)	3.43(0.49)	12.50(2.04)	8.54(1.69)	7.06(1.68)	16.30(1.97)	5.26(0.77)
	bulk minus dry	0.10(1.40)	4.26(0.53)	13.99(2.28)	-1.57(1.47)	-0.72(1.34)	8.96(1.42)	0.93(0.56)
				July 14				
petri dish	wet-only	3.39(0.29)	2.15(2.15)	5.87(0.19)	4.00(0.28)	0.76(0.47)	11.48(1.36)	3.18(0.46)
	dry-only	1.59(0.27)	2.15(0.15)	0.93(0.57)	2.87(0.74)	2.09(0.19)	54.44(10.37)	2.57(0.68)
	bulk minus dry	1.65(0.73)	1.08(0.35)	7.11(0.86)	-0.07(0.80)	-0.38(0.38)	11.11(10.19)	3.91(1.70)
maple leaf	wet-only	7.59(1.99)	1.75(0.19)	13.83(3.74)	2.09(0.41)	4.41(0.76)	18.49(2.58)	7.54(0.61)
	dry-only	1.95(0.10)	3.18(0.19)	10.65(4.59)	3.10(0.41)	2.29(0.23)	12.51(2.74)	4.80(0.71)
	bulk minus dry	2.87(0.39)	1.94(0.39)	2.35(3.68)	-0.62(0.61)	1.47(0.62)	8.79(2.12)	3.68(0.62)

Table 15 (continued).

Type of Surface	Treatment	Ion Concentration (ueq m^2)						
		Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}
				July 22				
petri dish	wet-only	8.39(1.31)	12.48(0.92)	20.86(0.91)	6.41(1.78)	3.80(1.13)	48.41(7.42)	9.64(1.71)
	dry-only	4.37(0.63)	1.20(0.93)	3.86(0.45)	4.73(0.78)	1.36(0.68)	49.20(4.41)	15.83(1.72)
	bulk minus dry	1.76(1.13)	11.37(2.00)	17.44(1.44)	1.08(1.08)	0.81(1.07)	3.44(8.37)	-5.28(2.75)
maple leaf	wet-only	6.37(0.61)	3.20(1.23)	14.00(3.25)	4.83(0.54)	5.17(1.22)	37.86(8.62)	13.69(3.70)
	dry-only	4.31(0.63)	8.01(1.16)	12.72(2.94)	6.00(0.68)	3.38(0.13)	42.95(2.47)	14.81(0.95)
	bulk minus dry	4.13(1.26)	3.21(1.56)	6.63(3.49)	1.19(1.01)	3.71(1.63)	12.51(5.13)	3.70(1.28)
				August 7				
petri dish	wet-only	2.41(0.88)	9.32(0.86)	14.68(0.67)	2.03(0.82)	1.49(0.54)	23.01(3.02)	12.08(1.98)
	dry-only	0.33(0.16)	4.96(0.45)	2.43(0.46)	0.19(0.12)	0.41(0.41)	22.48(0.85)	13.09(0.27)
	bulk minus dry	2.12(0.49)	5.56(0.85)	12.91(0.62)	1.55(0.58)	1.49(2.01)	2.12(2.37)	-0.65(1.72)
maple leaf	wet-only	3.33(0.32)	1.60(0.19)	4.98(0.40)	2.70(0.36)	3.24(0.50)	12.91(0.91)	4.64(0.32)
	dry-only	2.52(0.17)	10.29(1.84)	8.36(2.28)	2.48(0.18)	2.96(0.28)	22.87(3.20)	.46(1.05)
	bulk minus dry	3.71(0.53)	-2.68(1.27)	3.52(2.19)	0.74(0.68)	2.28(0.81)	4.34(2.24)	1.79(0.60)
				August 20				
petri dish	wet-only	0.99(0.29)	2.74(0.18)	6.95(0.63)	0.62(0.29)	1.36(0.50)	10.58(2.76)	7.94(0.44)
	dry-only	0.31(0.31)	6.67(0.77)	6.07(0.26)	0.67(0.43)	1.22(0.58)	27.25(1.55)	16.58(0.74)
	bulk minus dry	1.74(0.58)	-1.03(0.90)	5.30(0.59)	1.78(0.47)	2.98(0.56)	6.35(2.74)	1.53(1.87)
maple leaf	wet-only	4.67(0.24)	1.99(0.73)	11.16(3.70)	1.15(0.11)	4.31(0.61)	22.70(3.73)	7.65(1.24)
	dry-only	2.32(0.13)	6.08(0.74)	7.60(1.38)	1.68(0.15)	3.68(0.26)	20.02(1.53)	8.26(0.48)
	bulk minus dry	6.02(1.62)	-1.03(0.76)	6.49(4.07)	0.16(0.43)	1.54(0.84)	13.45(3.78)	4.66(1.47)

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Table 16. Three-way ANOVA for main effects, no leaf exchange (petri dishes) vs. leaf exhange (maple leaves) and no dry deposition (wet-only samples) vs. previous dry deposition (bulk-minus-dry samples), and interaction (leaf exchange x dry deposition). Significance levels: * P < .05, ** P < .01, *** P < .001, ns non-significant.

Date	Effect	Ion						
		Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
June 10	leaf exchange	ns	*	*	ns	ns**	*	
	dry deposition	***	ns	**	*	***	***	***
	interaction	***	ns	*	ns	***	*	*
June 18	leaf exchange	ns	ns	ns	ns	*	*	*
	dry deposition	ns	**	**	**	***	***	***
	interaction	ns	ns	*	*	***	*	ns
July 8	leaf exchange	ns	ns	ns	ns	ns	***	ns
	dry deposition	*	ns	ns	***	ns	***	*
	interaction	**	ns	*	**	ns	***	ns
July 14	leaf exchange	**	ns	ns	ns	***	ns	***
	dry deposition	*	ns	ns	***	**	ns	*
	interaction	ns	ns	ns	ns	ns	ns	*
July 22	leaf exchange	ns	***	**	ns	ns	ns	*
	dry deposition	***	ns	*	***	ns	***	***
	interaction	ns	ns	ns	ns	ns	ns	ns
August 7	leaf exchange	*	***	***	ns	ns	ns	ns
	dry deposition	ns	***	ns	ns	ns	***	***
	interaction	ns	ns	ns	ns	ns	*	***
August 20	leaf exchange	***	ns	ns	ns	ns	**	ns
	dry deposition	ns	***	ns	ns	ns	ns	**
	interaction	ns	ns	ns	**	**	ns	ns

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the greater duration of the dry periods in the rain experiment compared to the dew experiment (77-239 hr vs. 12 hr) may have "evened out" short-term fluctuations in aerosol deposition rates to dishes and leaves, such that, over the long-term, rates were identical for both surfaces; or (2) the probable occurrence of dews during the multi-day dry periods in the rain experiment may have altered leaf surface aerosol concentrations as ion exchange and diffusion occurred between dews and leaf interiors.

Net deposition of all of the ions we examined in dews occurred in the absence of previous dry deposition (Table 15). This result was a repeat of our observation that ion deposition occured to dew on chemically-inert Teflon as a result of gas absorption and concurrent aerosol sedimentation (see Chemistry of Dews). When previous dry deposition was absent, net K^+ and Cl^- deposition during dews was always greater to leaves than to petri dishes (Table 15). This may have been caused by efflux of these ions from leaves into dew. The variable results for other ions might have been the result of large leaf-to-leaf variability, as well as shifts from influx to efflux of ions among individual dew events. Our data cannot distinguish between these possibilities.

When previous dry deposition was present, deposition patterns were altered. Accumulation of SO_4^{2-}, NO_3^-, and Na^+ was always greater to petri dishes than to leaves (Table 15). Since less dry deposition of ions SO_4^{2-}, NO_3^-, and Na^+ occurred to dishes than to leaves, greater, not less, deposition should have occurred to dishes during dews when previous dry deposition existed. Since the dishes were chemically inert, there was no source for the "extra" ions. A more likely explanation was that fluxes of these ions occurred from dews into the leaves.

In summary, we found evidence for (1) net deposition of ions to leaves during dew events when pre-existing dry deposition was excluded; and (2) a strong influence of preexisting dry deposition on ion deposition by dews. The highly variable results among ions and between individual dew events suggested that multiple mechanisms acted to alter surface ion concentrations on leaves, and that leaf-to-leaf variability posed a major problem for field samping of leaf/dew chemical interactions.

ACID MIST AND FOLIAGE CHEMICAL INTERACTIONS IN THE LABORATORY

INTRODUCTION

To assess the effect on foliar chemistry from exposure to acidic wet deposition, a series of experiments using greenhouse-grown plants was conducted. The first experiment, using beet plants, assessed the effects of single and repeated exposures to acid mists on concentrations of elements in leaves and on the chemical properties of simulated acid mist droplets while residing on leaf surfaces. Mists were acidified with hydrochloric acid (HCl) to various pH values; therefore, this experiment evaluated the possible influence of single and multiple shuttle launches on vegetation nutrient status at varying distances from launch pads.

The second experiment, using pinto beans, compared the effects of pH and source of acidity (HCl vs. sulfuric/nitric acids) on foliar chemistry, changes in leaf surface droplet chemistry, and the ability of

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foliage to recover chemically from leaching events. We asked the question, "Is it acidity *per se* which drives chemical interactions between wet deposition and plants, or do the anions (Cl^-, SO_4^{2-}, NO_3^-) produced by acid dissolution also play a role?"

The third experiment, using tomato plants, examined the influence of varying levels of foliar chemistry on the chemistry of whole-plant throughfall resulting from HCl-acidified mist applications. This study examined the potential for shuttle launches at Vandenberg AFB to negatively impact nutrient status of plants growning on the nutrient-poor sand dune soils near the launch pad.

INFLUENCE OF SINGLE AND REPEATED EXPOSURES TO HCL-ACIDIFIED MISTS ON NUTRIENT LEACHING AND FOLIAR CHEMISTRY OF BEET PLANTS

Introduction

Exposure of natural vegetation to HCl-acidified wet deposition resulting from shuttle launches has to date been restricted to single events of several hours duration at Kennedy Space Center. With an expanded shuttle program, this scenario could change. Multiple launches could occur at the same site within as little as a week of each other. At Vandenberg AFB, with its high frequency of fog and dew, wet deposition could continue to scavenge HCl for several days after shuttle launches.

A series of experimental plant exposures using HCl-acidified mists was conducted during the winter of 1985-86 to examine the influence of various scenarios on foliar chemistry and on chemical interactions between wet deposition and leaf surfaces. Different pH values were used, because (1) the pH of shuttle launch wet fallout increases with increasing distance from launch pads (Potter 1983), and (2) several previous studies have shown that ion efflux from leaves to acidic surface moisture can be pH-dependent (see BACKGROUND). We expected that, with decreasing pH of applied mists, increased efflux of elements would occur from foliage, as indicated by increasing concentrations of ions in leaf surface droplets and foliar washates. Furthermore, if sufficient efflux occurred, decreases in foliage element concentrations might occur.

Methods

Plant Culture. The experiment was conducted during the winter and spring of 1986. Beet (*Beta vulgaris*) plants were chosen because they may be more sensitive to acid deposition than leaf and fruit crops (Jacobson 1984), and because they have intermediate tolerance to HCl gas (Granett and Taylor 1981). Plants were grown in clay pots, three plants per pot, in a 2:1:1 mixture of potting soil, sand, and vermiculite under natural light, and were tap-watered daily. When the plants were approximately 12 cm tall, pots were randomly assigned to each of five pH treatments for a total of 30 plants per treatment. Plants were moved to the HRI laboratory and maintained at room temperature without artificial light for the duration of the experiment.

<u>Single Exposure to Acid Mist</u>. The first experiment determined whether or not a single acid mist treatment had immediate and measurable effects on foliar chemistry. When plants were two months old, the ten pots in each pH treatment were placed in a tray over which a clear plastic tent was erected. Distilled, deionized water was acidified with HCl to pH 1, 2, 3, or 4, or left unacidified (pH 5.6) as a control. These acidities were within the range of pH values reported for droplets in the immediate vicinity of the launch pad at Kennedy Space Center (Potter 1983) and in rain, fog, and dew from around the world (see BACKGROUND).

Simulated acid mists were delivered to the plants with plastic, hand-held sprayers starting at 1000 hr. Foliage was misted until it was thoroughly wet but not dripping. After 1 hr, droplets on leaf surfaces were collected using plastic syringes and were pooled in plastic sample bottles to provide sufficient volume for chemical analysis. The plants were sprayed again and a second droplet collection was made 1 hr after that spraying. A total of approximately 30 mL of water was applied to each plant during the two sprayings.

Three collections of foliage from plants in each pH treatment were made after the mist had dried. These collections occurred 3, 4, and 5 hr, respectively, after the second spraying. At each collection, five leaves were removed randomly from the 30 plants in each pH treatment, using plastic gloves. Leaves were refrigerated overnight in Ziploc bags. The next day, each set of leaves was rinsed free of surface ions by shaking for 2 min in 25 mL of distilled, deionized water in a 500-mL plastic bottle. The pH of the washates was promptly measured, and the foliage samples were oven-dried and stored in paper bags. Droplet samples were analyzed for cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) and leaf washate samples were analyzed for both cations and anions (SO_4^{2-}, NO_3^-, PO_4^{3-}).

<u>Repeated Exposures over a Two-Week Period</u>. Six weeks after the first experiment, the same set of beet plants was subjected to a second set of acid mist treatments. Using the same mist pH values as in the first experiment, plants were sprayed at hourly intervals for 3 hr, starting at 1000 hr, for a total of approximately 190 mL of applied water per plant. To simulate multiple, closely-spaced shuttle launches, this procedure was repeated 1, 7, and 14 days after the first set of mistings. One hour after the end of mist treatments on each day, droplets were collected from leaf surfaces in the same manner as the first experiment. After the final day of mist treatments, foliage was collected after the leaf surfaces had dried. As with the first experiment, each collection consisted of five leaves randomly removed from each set of experimental plants. However, the three collections occurred in rapid sequence, rather than at hourly intervals. Leaf washings and chemical analyses occurred as described for the first experiment.

<u>Repeated Exposures on Four Successive Days</u>. The third experiment used the same plants as the first two experiments, starting one month after the second experiment. Exposure to acid mists followed the same methods, but occurred on four successive days, with spraying occurring at four hourly intervals on each day, starting at 1000 hr. Approximately 150 mL of water was applied per plant each day. This procedure simulated several successive days of exposure to acidic fog, rain, or dew following a shuttle launch.

Leaf surface droplets were collected 1 hr after the final spraying each day, promptly analyzed for pH, and both cation and anion concentrations measured. On the fourth day, foliage was collected after leaves had dried, then was rinsed and chemically analyzed following the same procedures as the first two experiments.

Statistical Analyses. Droplet chemistry was not subject to statistical analysis in the absence of replication. This was a consequence of the need to pool large numbers of droplets to produce sufficient volume for chemical analysis. Differences in leaf washate and foliar chemistry were compared between collection times and across pH treatments using ANOVA, on SPSS software (Hull and Nie 1981).

Results

Single Exposure to Acid Mist. Droplets on leaf surfaces contained substantial amounts of cations (Table 17). The concentrations of K^+ and Ca^{2+} increased with decreasing pH, while those of Mg^{2+} and Na^+ showed no relation to pH. Within each pH treatment, cation concentrations in droplets decreased in the following order: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ (Table 17). Sample volumes were too small to analyze for anions.

Foliar washates contained higher concentrations of Ca^{2+} and Mg^{2+} than did droplets, as well as substantial concentrations of SO_4^{2-} and NO_3^- (Table 18). Washate ion concentrations were not influenced by either pH treatment or time of collection (ANOVA, minimum P = .16).

There were no significant differences in foliar concentrations of Ca, Mg, or Na in as a function of pH or time of collection (minimum P = .06), but there was a significant pH effect for K (Table 19). Although K concentration was less with the pH 4 than with the pH 5.6 treatment, it increased as pH decreased from 4.0 to 1.0 (Table 19).

Repeated Exposures over a Two-Week Period. No one cation showed a trend in leaf droplet concentration with respect to pH treatment on any of the four days (Table 17). At a given pH, Ca^{2+} concentrations decreased between successive spray dates, but no temporal pattern was apparent for the other cations (Table 17).

Potassium and NO_3^- concentrations in foliar washates were significantly affected by mist pH (ANOVA, P < .01; Table 18). In the case of NO_3^-, concentration decreased as pH decreased, while for K^+, concentration was greatest in the pH 1.0 and 5.6 treatments. Washate concentrations of other cations and anions were not influenced by mist pH (Table 18).

As with the first experiment, foliar element concentrations were not influenced by mist pH or by time of collection (ANOVA, minimum P = .10; Table 19).

Repeated Exposures on Four Successive Days. On the first, second, and fourth days, leaf surface droplet pH increased after contact with foliage, with the magnitude of the increase becoming greater as pH decreased from 5.6 to 2 (Table 20). On the third day, pH increased with the pH 4 and 6 treatments, but

Table 17. Ion concentrations in leaf surface droplets following various exposures to mists acidified with HCl.

Day	Mist pH	Ion Concentration (mq L^{-1})			
		K^+	Ca^{2+}	Mg^{2+}	Na^+
		Single 2-hr Exposure			
1	1.0	4.17	127	32.2	5.46
	2.0	3.94	120	35.5	6.46
	3.0	3.04	66.5	32.7	6.25
	4.0	3.04	57.5	27.0	5.54
	5.6	4.82	80.3	37.3	8.03
		Four 4-hr Exposures, Several Days Apart			
1	2.0	0.90	33.4	7.23	0.68
	3.0	2.0	32.6	14.5	0.97
	4.0	1.7	25.7	7.78	0.56
	5.6	2.4	32.4	12.1	1.1
2	2.0	0.70	20.5	4.22	0.24
	3.0	0.63	15.4	3.41	0.19
	4.0	0.99	17.1	4.85	0.72
	5.6	1.31	20.8	4.16	0.30
3	2.0	1.97	18.2	4.64	0.91
	3.0	1.51	25.7	5.98	0.69
	4.0	0.78	10.4	2.73	0.61
	5.6	1.69	18.8	4.00	0.47
4	2.0	2.61	6.83	2.30	0.92
	3.0	0.97	11.1	1.55	0.45
	4.0	8.02	8.29	3.38	3.47
	5.6	3.48	7.82	1.96	0.88
		Four 4-hr Exposures On Successive Days			
1	1.0	103	80.9	21.6	18.9
	2.0	11.8	18.8	5.66	2.39
	3.0	8.43	14.8	5.02	2.25
	4.0	12.5	12.1	4.83	1.76
	5.6	41.3	13.3	5.20	7.52
2	1.0	660	51.2	69.3	126
	2.0	10.6	19.9	4.00	2.00
	3.0	4.49	15.3	2.20	0.86
	4.0	23.0	14.2	3.80	5.27
	5.6	71.7	9.90	7.19	15.2
3	1.0	1038	26.6	79.7	172
	2.0	7.93	10.8	2.54	1.40
	3.0	5.83	9.70	1.12	0.99
	4.0	6.52	5.41	1.21	1.19
	5.6	6.09	6.84	1.55	1.53
4	1.0	2392	50.7	1250	3702
	2.0	14.3	9.59	2.73	2.32
	3.0	5.64	8.00	0.89	1.46
	4.0	6.60	9.38	1.49	1.25
	5.6	10.2	3.92	1.19	1.72

Table 18. Ion concentrations in washates from beet leaves following various exposures to exposures to mists acidified with HCl. Data are normalized to dried leaf mass for each plant.

Mist pH	K^+	Ca^{2+}	Mg^{2+}	Na^+	SO_4^{2-}	NO_3^-	Cl^-
			Ion Concentration (mq kq^{-1} dry leaf mass)				
				Single 2-hr Exposure			
1.0		442(118)	94(27)		483(147)	25 (9)	2621(463)
2.0		394 (62)	79 (3)		441 (16)	37(12)	436 (82)
3.0		417 (84)	92(29)		449(144)	37(14)	150 (63)
4.0		487 (38)	99(11)		559 (91)	41(10)	105 (31)
5.6		553 (74)	125(19)		651 99)	49(17)	121 (48)
				Four 4-hr Exposures, Several Days Apart			
2.0	33 (5)	56 (11)	13 (1)	10 (4)	82 (10)	2 (1)	101 (8)
3.0	22 (2)	71 (35)	12 (4)	7 (1)	59 (19)	4 (1)	50 (12)
4.0	22 (3)	86 (54)	14 (6)	6 (2)	59 (41)	6 (1)	31 (2)
5.6	30 (4)	88 (33)	15 (3)	8 (2)	58 (22)	6 (1)	27 (1)
				Four 4-hr Exposures On Successive Days			
1.0	1954(276)	79 (3)	271(27)	669(75)	537 (80)		4560(283)
2.0	33 (29)	19 (3)	13 (4)	11 (7)	23 (5)		87 (36)
3.0	13 (12)	30 (30)	9 (3)	3 (3)	40 (37)		21 (8)
4.0	18 (10)	37 (11)	10 (2)	4 (2)	8 (2)		38 (14)
5.6	25 (8)	72 (32)	23 (3)	6 (3)	73 (72)		37 (1)

Table 19. Element concentrations in beet leaves following various excposures to mists acidified with HCl.

Mist	Concentrations (g kg^{-1}) dry leaf mass			
pH	K	Ca	Mg	Na
Single 2-hr Exposure				
1.0	40.3(3.6)	14.5(0.8)	11.6(1.1)	32.6(5.2)
2.0	39.5(2.3)	16.0(1.6)	12.7(1.1)	36.2(1.4)
3.0	43.9(8.4)	17.2(2.6)	13.6(0.5)	31.4(7.7)
4.0	32.0(2.3)	16.4(3.4)	11.0(0.7)	30.6(1.3)
5.6	45.9(1.6)	13.8(0.7)	12.1(1.2)	33.6(5.4)
Four 4-hr Exposures, Several Days Apart				
2.0	52.5(3.2)	23.1(4.9)	9.2(0.6)	
3.0	55.4(2.5)	17.7(1.4)	10.1(0.9)	
4.0	52.5(1.9)	21.3(7.7)	9.8(3.1)	
5.6	59.3(0.7)	21.8(3.7)	10.2(1.0)	
Four 4-hr Exposures on Successive Days				
1.0	50.4(3.6)	23.3(2.0)	9.8(0.5)	18.4(3.6)
2.0	51.6(6.7)	25.1(7.6)	8.3(1.4)	20.4(0.5)
3.0	51.3(4.8)	19.3(0.8)	9.0(0.6)	16.5(1.6)
4.0	52.7(1.9)	19.2(0.5)	8.6(0.9)	16.2(1.1)
5.6	50.5(2.9)	21.9(3.9)	8.7(0.6)	17.5(0.5)

Table 20. pH of droplets collected from beet leaf surfaces after exposure to 4 hr of mists acidified with HCl.

Mist	Day			
pH	1	2	3	4
1.0	0.97	1.09	0.93	0.97
2.0	2.07	2.04	1.82	2.00
3.0	3.92	3.20	2.92	3.10
4.0	5.19	6.50	5.93	5.45
5.6	5.89	6.73	6.87	5.66

decreased at lower pH. Droplet pH either increased or decreased at pH 1 (Table 20).

The concentration of Ca^{2+} in droplets increased with decreasing pH on all days (Table 17). For other cations and anions, the concentration patterns were more variable, but pH 1 droplets always contained much higher ion concentrations than did droplets of higher pH (Table 17).

By the end of the fourth consecutive day of spraying, leaves subject to pH 1 mists were dead. Not surprisingly, large amounts of elements from these leaves were found in washates, making the pH effect on washate ion concentrations highly significant (ANOVA, all P values < .001; Table 18). If pH 1 values were excluded from the ANOVA's. Ca^{2+} and Mg^{2+} concentrations decreased signficantly as pH decreased (P = .05 and .002, respectively; Table 18). Nitrate and PO_4^{3-} were detected only in washates from pH 1 treatments.

There was no influence of mist pH treatment on foliar element concentrations (minimum P = .11) if all treatments were included (Table 19). If pH 1 leaves were excluded from the ANOVA, Na concentration increased significantly as pH decreased (P = .004).

Discussion

This series of experiments did not indicate that efflux of ions from foliage into acidified mists was a predictable function of mist pH. For example, droplet Ca concentrations increased, decreased, or showed no pattern with respect to mist pH. Ion concentrations in leaf washates diminished between successive mistings in the second and third experiments, suggesting depletion of foliar nutrient pools. However, there was no indication of such depletion based on direct elemental analyses of leaves. This does not rule out such depletion for individual mistings. The results were subject to two confounding influences: (1) ontogenetic changes in foliar element concentrations as plants aged, and (2) potential recovery of plant element contents between mistings.

We did not account for the presence of previously deposited aerosols on leaf surfaces, which could mean that much of the ion concentration behavior we observed in droplets and leaf washates was attributable to aerosols going into solution rather than ion efflux from leaves. It was also possible that ion efflux into HCl-acidied mists was not as great as into sulfuric/nitric acid-acidified mists at a given pH.

INFLUENCE OF PH AND SOURCE OF ACIDITY ON SURFACE DROPLET AND LEAF CHEMISTRY OF PINTO BEANS EXPOSED TO SIMULATED ACID MISTS

Introduction

During the winter of 1986-87, a new set of misting experiments was conducted, with three objectives: (1) to examine the influence of mist pH on ion efflux/influx between leaf surface droplets and leaf interiors: (2) to measure temporal patterns of foliar ion efflux/influx during the course of individual mistings; (3) to compare the efficacy of acidity source (HCl vs. $H_2SO_4 + HNO_3$) in causing foliar ion efflux/influx; (4) to study the influence of mist pH and source of acidity on foliar chemistry; and (5) to determine whether or not "recovery" of elements leached from leaves occurred following acid mist exposures. Aerosol contamination

of leaf surfaces was minimized, thus overcoming a major drawback of the previous experiment with beets.

Methods

Plant Culture. We chose pinto bean (*Phaseolus vulgaris* var. *pinto*) as the experimental species because: (1) it is relatively sensitive to HCl in both gaseous and mist forms (Granett and Taylor 1981); (2) it develops visible and microscopic foliar injury (Evans et al. 1977) when exposed to mists or rains of low pH; (3) its foliar surfaces have been observed to partly neutralize acid water droplets (Adams and Hutchinson 1984, Craker and Bernstein 1984); and (4) previous research found that leaching rates of some elements from its foliage were pH-dependent (Wood and Bormann 1975).

Plants were raised from seed in two growth chambers at $26^{\circ}C/21^{\circ}C$ day/night temperature, and a 16-hr photoperiod provided by fluorescent and incandescent lamps. The chambers were thoroughly washed beforehand and had recirculating air, thus minimizing aerosol contamination. Individual seeds were grown in a sterilized 2:1:1 mix of potting soil, sand, and vermiculite in clay pots. Plants were bottom-watered with tap water at regular intervals. One week after seedling emergence, plants were fertilized with Ortho Fish Emulsion fertilizer.

The experiment commenced when the beans were s⁞ weeks old and had three or more fully expanded, trifoliate leaves. Plants were randomly assigned to mist treatments the day before each misting began. Plant stems were supported by plastic rods, to keep them from drooping and contacting the soil during misting. The soil surface was covered tightly with plastic taped to the plant's stem to ensure that the mists could not reach the soil via stem flow. After each misting, plants were returned to the growth chambers.

Mist Treatments. Distilled, deionized water was acidified to pH 2.5 and 4.0 using either HCl or a 2:1 ratio (equivalent basis) of H_2SO_4 to HNO_3; pure water served as a control. The 2:1 ratio was similar to that commonly observed in ambient rainfall in the eastern United States. pH 4.0 was at the low end of median pH values for rainfall in the eastern United States, while pH 2.5 was near the low end of observed pH of fogs (see Tables 1 and 2).

Mists were applied in three 0.8-m wide, 1.2-m tall, rectangular polyethylene mist chambers, using one stainless steel impingement nozzle (Bete Fog Nozzle model PJ-10) per chamber. These nozzles delivered a large proportion of droplets at diameters less than 50 μm. Nozzles were mounted 1 m above the plants, pointing upward. Water was delivered to the nozzles by Teflon tubing from stainless steel tanks pressurized to 27.6 Pa. Flow rates were approximately 1.5 L h^{-1} to each chamber. Plants were placed on a turntable inside each chamber that rotated at 5 rpm to ensure that similar volumes of mist were applied to each plant.

Nine plants were assigned to each of the six pH/acid source treatments. Plants were misted three times for 4 hr each time (between 1000 and 1400 hr) at 72-hr intervals. Forty-eight hours prior to the first misting, each plant was misted for 30 min with distilled, deionized water in the misting chambers to remove

surface aerosol contamination. To minimize chamber effects, different chambers were used for each pH treatment during each misting day. Between mistings, plants were returned to the growth chambers.

Droplets were collected from the upper surfaces of the lower three trifoliates on each plant at regular intervals during each misting, using plastic syringes, and were placed in clean plastic sample bottles. The nozzles were shut off for 1 min before each collection to ensure that all droplets had been in contact with foliage for at least 1 min. Droplet collections, lasting 10 min each, occurred at 5, 30, 60, 120, 180, and 240 min after the start of each misting. Three composite samples of droplets from three separate plants in each group of nine plants were prepared to ensure sufficient volume for chemical analysis.

Immediately after the final misting, the upper and lower surfaces of the lower three trifoliates on each plant were rinsed thoroughly with distilled, deionized water and four or five leaflets were removed as a composite sample, using plastic gloves. The plants were returned to the growth chambers, and 72 hr later the remaining leaflets from the lower three trifoliates were removed. The leaflets were dried and analyzed for element (K, Ca, Mg, Na) concentrations. An additional leaflet collection was made from four plants that had received no mistings to serve as a control for misting effects.

Leaf Element Recovery. Following the completion of the first series of experiments, 48 pinto beans were grown in the same manner as described above. At one month of age, the plants were misted for 30 min with distilled, deionized water in the misting chambers to remove dry-deposited particles from the leaf surfaces, then put back in the growth chambers for 24 hr. Then the plants were subjected to 4-hr mistings at either pH 2.5 or 5.6, using the same procedure as described above, except that the misting nozzles pointed downward from the top of each chamber. This increased the water deposition rate somewhat, but prevented any contamination from water dripping off the plastic walls of the chambers. Only 24 plants could be misted at one time. Therefore, one-half of the plants received treatments right away, and the other half received treatments 24 hr later.

At the end of each misting, the upper and lower surfaces of the lower four trifoliates on each plant were rinsed with distilled, deionized water, using a plastic spray bottle. The lower four trifoliates were immediately harvested (excluding petioles) from six plants of each pH treatment, placed in clean paper bags, oven-dried, and analyzed for element (K, Ca, Mg, Na) concentrations. The remaining plants were returned to the growth chambers for leaf removal after 12, 36, or 72 hr (six replicate plants for each pH/time combination). Allocation of plants to treatments, chambers, and days was random.

Statistical Analyses. Analyses of the influence of between-subjects factors (pH and source of acidity) and within-subjects factors (collection time within each misting session and different misting days) on droplet and foliar chemical concentrations utilized repeated measures ANOVA in SPSS software (Hull and Nie 1981). Date and time were transformed using orthogonal contrasts. To compare different mistings, the mean cation concentrations were calculated for each of the six collections within each session, with each collection mean being weighted by the time elapsed since the preceding droplet collection. Paired t-tests

assessed the effects of immediate and delayed (72-hr) collections on leaf foliar chemistry.

The influences of mist pH, recovery time (0, 12, 36, or 72 hr), and pH x time interaction in the final experiment on leaf element recovery were analyzed with a two-way, factorial ANOVA using SYSTAT software (Wilkinson 1984).

Results

Visual Injury. Lesions appeared on the upper surfaces of leaflets on most plants treated with pH 2.5 mists (either acidity source) within 24 hr of the first misting session. Lesions were present on all plants by the start of the second misting and the number and size of lesions increased with further mistings. By the end of the third misting, lesions covered 1-5% of the upper leaflet surfaces on all plants. There were no apparent differences in lesion size, number, or appearance between HCl and $H_2SO_4 + HNO_3$ mists, although quantitative comparisons were not made.

Droplet Chemistry. The source of acidity did not affect Ca^{2+} and Mg^{2+} concentrations between days or between times within each day (minimum P from ANOVA = .14), but did exert a significant (P < .05) influence on Na^+ concentrations between days and between times within the first day, and on K^+ concentrations between times within the first and third days (Table 21). On the first day, K^+ and Na^+ concentrations were significantly higher in droplets from leaves treated with HCl mists than from those treated with $H_2SO_4 + HNO_3$ mists (P = .036 for both cations). On the third day, K^+ concentrations were significantly higher in $H_2SO_4 + HNO_3$ droplets than in HCl droplets (P = .010; Table 21).

Concentrations of K^+, Ca^{2+}, and Mg^{2+} decreased significantly with increasing pH, regardless of source of acidity, on all days (maximum P = .01), except for HCl mists on the first day (P = .10 and .29 for Ca^{2+} and Mg^{2+}, respectively; Table 21). All pH values showed significant differences for Ca^{2+}, but pH 4.0 and 5.6 did not differ significantly for Mg^{2+} on any day. For K^+, pH 4.0 and 5.6 sometimes differed significantly, with pH 4.0 either higher or lower than pH 5.6. Sodium concentrations were never significantly influenced by pH (minimum P = .06; Table 21).

The responses of K^+, Ca^{2+}, and Mg^{2+} concentrations to day, time, and pH are shown in Figure 5. Because source of acidity did not affect effect Ca^{2+} and Mg^{2+} concentrations and had little effect on K^+ concentrations, and the concentrations of these ions did not differ between pH 4.0 and 5.6 mists (see above), only results for pH 2.5 and 4.0 for HCl mists are shown. Concentrations of Ca^{2+} and Mg^{2+} at either pH generally decreased significantly with time within each day. For both ions, concentrations did not differ significantly between pH 2.5 and 4.0 on the first day, but pH 2.5 concentrations were significantly higher at all times on the second and third days, with the largest differences on the third day (Fig. 5). Calcium and Mg^{2+} concentrations decreased during the first 2 hr on the first day and remained more or less constant with time on the second day; on the third day, Ca^{2+} concentration declined steeply during the first 2 hr at

Table 21. Cation concentrations (mg L^{-1}) in droplets collected from misted leaves. Data are means (± 2 standard errors) for the six collection intervals within each spray date.

Cation	Day 1		Day 2		Day 3	
	HCl	H$_2$SO$_4$+HNO$_3$	HCl	H$_2$SO$_4$+HNO$_3$	HCl	H$_2$SO$_4$+HNO$_3$
pH 2.5						
Calcium	0.835(0.300)	0.806(0.370)	0.743(0.081)	0.942(03.81)	2.317(0.994)	3.540(0.815)
Magnesium	0.248(0.089)	0.187(0.093)	0.242(0.069)	0.266(0.097)	0.620(0.252)	1.219(0.943)
Potassium	0.887(0.271)	0.662(0.138)	0.974(0.388)	1.375(0.393)	1.946(0.609)	3.932(0.932)
Sodium	0.085(0.107)	0.028(0.049)	0.001(0.002)	0.002(0.005)	0.004(0.006)	0.006(0.009)
pH 4.0						
Calcium	0.688(0.483)	0.381(0.275)	0.097(0.080)	0.123(0.163)	0.086(0.038)	0.109(0.126)
Magnesium	0.187(0.136)	0.098(0.067)	0.025(0.018)	0.041(0.036)	0.021(0.017)	0.044(0.042)
Potassium	1.209(0.320)	0.614(0.068)	0.311(0.084)	0.611(0.139)	0.405(0.121)	0.473(0.130)
Sodium	0.104(0.124)	0.040(0.078)	0.000(0.000)	0.001(0.002)	0.000(0.000)	0.001(0.002)
pH 5.6						
Calcium	0.187(0.140)	0.081(0.087)	0.063(0.053)	0.115(0.127)	0.069(0.097)	0.109(0.126)
Magnesium	0.048(0.034)	0.022(0.027)	0.028(0.019)	0.047(0.041)	0.032(0.039)	0.021(0.022)
Potassium	0.369(0.052	0.243(0.018)	0.417(0.166)	0.492(0.119)	0.250(0.041)	0.338(0.094)
Sodium	0.013(0.025)	0.008(0.016)	0.009(0.006)	0.003(0.006)	0.003(0.004)	0.006(0.009)
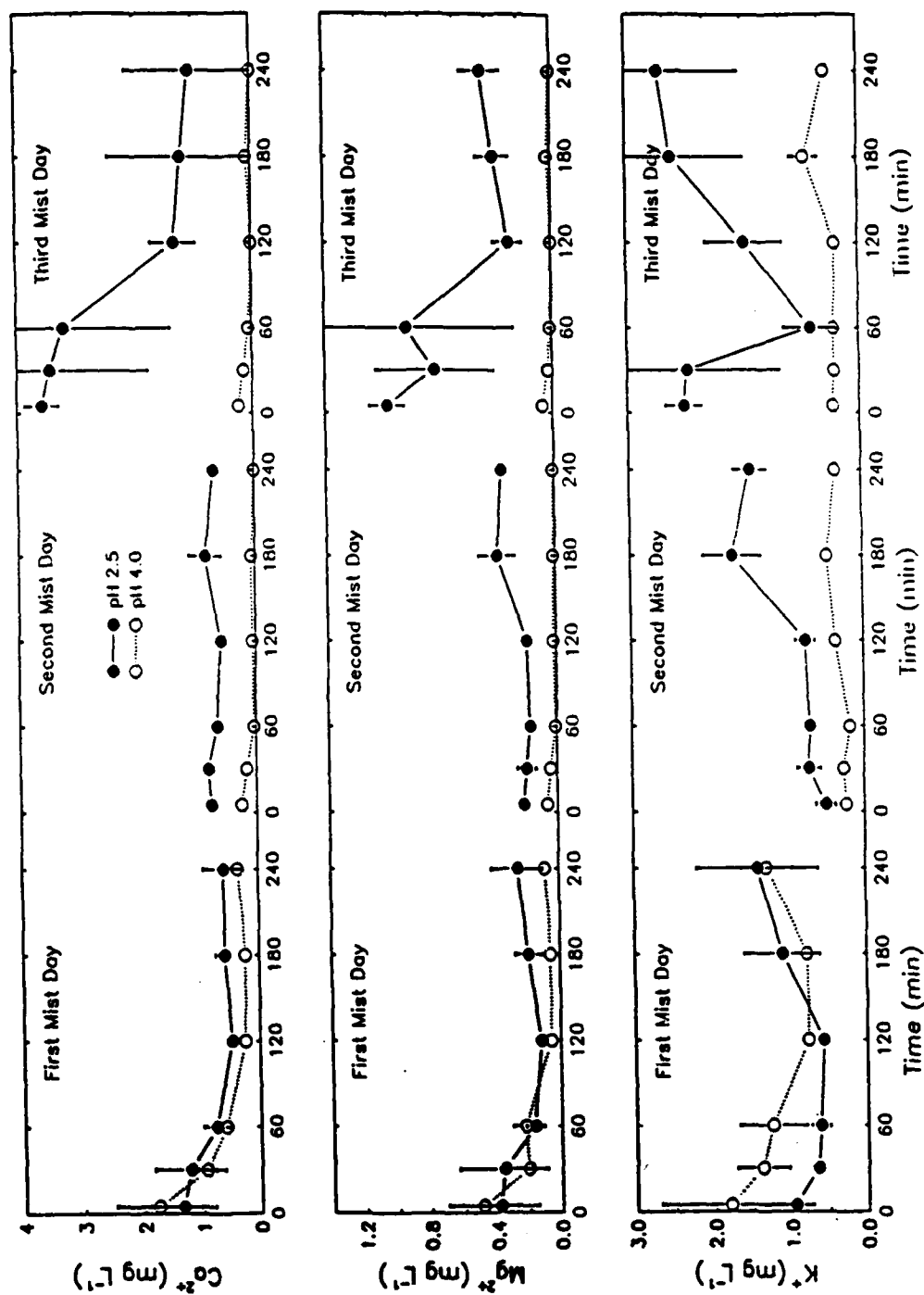
Figure 8. Mean (± 1 standard error) concentrations of calcium, magnesium, and potassium in leaf surface droplets on three successive days of four-hour exposures to mists acidified with HCl. Time of sampling is cumulative since the start of each misting.

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pH 2.5, but showed little temporal change at pH 4.0 (Fig. 5). Initial (5 min) Ca^{2+} and Mg^{2+} concentrations on the second day did not differ from final (240 min) concentrations on the first day, but a large jump in concentrations occurred between 240 min on the second day and 5 min on the third day (Fig. 4).

Potassium concentrations were affected significantly by time only for HCl mists on the first day and for both sources of acidity on the third day (P < .04; Fig. 5). Concentrations at pH 2.5 were significantly less than those at pH 4.0 during the first 60 min on the first day, significantly greater at all times during the second day, and significantly larger at all times except 60 min on the third day (Fig. 4). Concentrations of Na^+ generally reached zero within the first 2 hr of misting on the first day for both acids and all pH values, and stayed at or near zero for the remaining 2 hr.

Time had no effect on droplet pH within any day, nor was droplet acidity affected by contact with foliage on any day, irrespective of mist pH and acid source (Table 22). In contrast to this result, droplet acidity for the pH 4.0 mists decreased for both sources of acidity on all days except the third day with HCl, and for pH 5.6 mists droplet acidity increased with both sources of acidity on all days except for the first day with $H_2SO_4 + HNO_3$ (Table 22).

Foliar Chemistry. The source of acidity did not significantly affect foliar Ca^{2+} concentrations at any pH or collection time (initial vs. 72 hr; minimum P from ANOVA = .10), but did affect foliar concentrations of the other cations (Table 23). Both Mg^{2+} and K^+ concentrations were higher in foliage treated with $H_2SO_4 + HNO_3$ mists at the 72-hr collection (P = .03 and .01, respectively). Sodium concentrations were higher in foliage treated with $H_2SO_4^+ HNO_3$ mists than in foliage treated with HCl mists in the initial collection, while the reverse was true in the 72-hr collection (maximum P = .04; Table 23).

Foliar Ca^{2+} and Na^+ concentrations were significantly affected by mist pH for $H_2SO_4 + HNO_3$ mists in the initial collection and for HCl mists in the 72-hr collection (P < .04; Table 23). However, the trends in these ions' concentrations with decreasing pH differed between initial and 72-hr collections. Foliar K^+ and Mg^{2+} were not affected by mist pH except for HCl mists in the initial collection, when Mg^{2+} concentrations were much higher at pH 2.5 than at pH 4.0 (P = .05; Table 23).

Nonmisted foliage had significantly lower Ca^{2+} concentrations than foliage subject to pH 2.5 and 5.6, $H_2SO_4 + HNO_3$ mists in the initial collection, or than foliage subject to pH 2.5 and 4.0, HCl mists in the initial collection (P < .05; Table 23). Sodium concentrations were significantly higher in nonmisted than in misted foliage, regardless of mist pH, at 72 hr (P < .05). Magnesium concentrations did not differ significantly (minimum P = .34) between misted and nonmisted foliage except that they were higher for the pH 5.6, $H_2SO_4 + HNO_3$ treatment in the initial collection. Potassium concentrations never differed (P $\geq$ .29) between misted and nonmisted foliage (Table 23).

In general, foliar concentrations did not differ significantly between initial and 72-hr collections. The exceptions were K^+ and Na^+ for pH 4.0, $H_2SO_4 + HNO_3$ mists and Ca^{2+} and Na^+ for pH 5.6, HCl mists (Table 23).

Table 22. pH of droplets collected from leaves treated with acidic mists. Dat are means (± 2 standard errors) for the six collection intervals within each spray date.

Date	Source of Acidity	
	HCl	$H_2SO_4 + HNO_3$
	pH 2.5	
First	2.48(0.01)	2.49(0.03)
Second	2.52(0.01)	2.53(0.01)
Third	2.54(0.01)	2.52(0.01)
	pH 4.0	
First	4.14(0.07)	4.19(0.09)
Second	4.04(0.02)	4.08(0.03)
Third	4.00(0.05)	4.05(0.02)
	pH 5.6	
First	5.44(0.15)	5.63(0.16)
Second	5.44(0.12)	5.56(0.13)
Third	5.25(0.11)	5.41(0.13)

Table 23. Element concentrations in dried foliage (g kg^{-1}) after treatment with mists of different pH, and in non-misted controls. Data are means (± 2 standard errors) for foliage collected immediately after the final misting (initial) or 72 hours later ("72-hr").

Cation	Mist Treatment						
	pH 2.5		pH 4.0		pH 5.6		
	HCl	$H_2SO_4 + HNO_3$	HCl	$H_2SO_4 + HNO_3$	HCl	$H_2SO_4 + HNO_3$	non-misted
	Initial Collection						
Calcium	24.4(23.9)	27.1(32.4)	31.9(15.1)	23.2(2.5)	17.6(2.6)	28.5(2.7)	17.7(4.3)
Magnesium	56.1(0.4)	6.09(0.68)	5.38(0.56)	5.24(0.50)	5.27(0.44)	6.04(0.63)	4.91(0.43)
Potassium	23.4(3.7)	20.8(4.2)	21.2(2.5)	21.6(2.1)	23.7(1.0)	20.5(3.0)	(26.0(5.7)
Sodium	0.24(0.10)	0.26(0.05)	0.28(0.09)	0.51(0.14)	0.46(0.2)	0.33(0.12)	0.56(0.27)
	72-hr Collection						
Calcium	26.5(3.2)	35.1(10.6)	22.9(1.8)	25.5(7.2)	21.9(1.8)	22.9(7.0)	(15.6(3.0)
Magnesium	6.10(0.57	8.30(2.30)	5.49(0.57)	6.59(1.74)	5.18(1.06)	5.92(1.88)	5.80(2.93)
Potassium	22.9(2.',	31.0(9.1)	19.9(5.8)	28.0(2.6)	25.9(2.5)	25.4(8.5)	(32.0(12.7)
Sodium	0.24(0.06)	0.20(0.04)	0.29(0.10)	0.19(0.03)	0.17(0.03)	0.19(0.07)	(0.54(0.19)

<u>Leaf Element Recovery</u>. There was no significant change (P > .05) in foliar K, Ca, or Mg concentrations over time; however, Na concentrations declined significantly (P < .001) between 0 and 12 hr, then remained constant (Fig. 6). Concentrations did not differ between mist treatments for any ion at any recovery time (Fig. 6). The pH x time interaction was marginally significant (P = .045) for Ca.

Discussion

Decreases in cation droplet concentrations with time on the first day (Fig. 5) were much smaller than have been observed in other laboratory misting studies (Lovett and Lindberg 1985, Olsen et al. 1985) or in our leaf-washing kinetics studies (Muir et al. 1986, Appendix B), suggesting that our prerinsing procedure removed most surface aerosols. Similar to Wood and Bormann's (1975) whole-plant throughfall studies with pinto beans, we found no effect of mist pH on droplet Na^+ concentrations (Table 15). However, Wood and Bormann observed very large increases in K^+, Ca^{2+}, and Mg^{2+} concentrations as mist pH decreased during a single misting, whereas we noted large differences only during a third successive misting, and only between pH 2.5 and 4.0 (Fig. 5).

Droplet neutralization was small or nonexistent in this experiment; slight acidification occurred with some treatments (Table 22). This result contrasted sharply with those of Scherbatskoy and Klein (1983), who analyzed whole-plant throughfall from simulated acid mists (pH 2.8, 4.3, and 5.7) applied to spruce and birch seedlings. Even after three successive mistings (5-hr duration, 72 hr apart), most samples showed neutralization of 0.1-0.5 pH units.

It was unlikely that solubilization of leaf surface aerosols contributed substantially to observed droplet ion concentrations. The decline in concentrations during the first 60 min was slight for K^+, Ca^{2+}, and Mg^2, and nonexistent for Na^+ (Fig. 5). In contrast, "contaminated" leaves showed a sharp drop in cation concentrations, including Na^+, in leaf washing kinetics experiments (Lovett and Lindberg 1985, Muir et al. 1986b).

The role of ion exchange between H^+ and other cations on leaf surfaces, or within the leaf apoplast as a mechanism to account for cations appearing in droplets, was unclear. The higher concentrations of K^+, Ca^{2+}, and Mg^{2+} in pH 2.5 mists compared to pH 4.0 and 5.6 mists on the second and third days (Fig. 5) suggested that this mechanism was important, because the higher the concentration of H^+ ion (lower pH), the more ion exchange should have occurred. However, cation concentrations did not differ between pH 4.0 and 5.6 mists (Table 21) and there was only a small effect of contact with leaf surfaces on the pH of applied mists, with some droplets acidified rather than neutralized (Table 22). These results suggested that ion exchange was not important.

A third mechanism which may have contributed to the appearance of cations in droplets was diffusion of ions between droplets and the leaf apoplast. This could have accounted for the higher droplet Ca^{2+} and Mg^{2+} concentrations observed during the first collection time on the first and third days, but the lack of change with time in these ions' concentrations on the second day, and the anomalous behavior of K^+, left the importance of ion diffusion in doubt (Fig. 5). Active (energy-requiring) absorption or excretion of ions
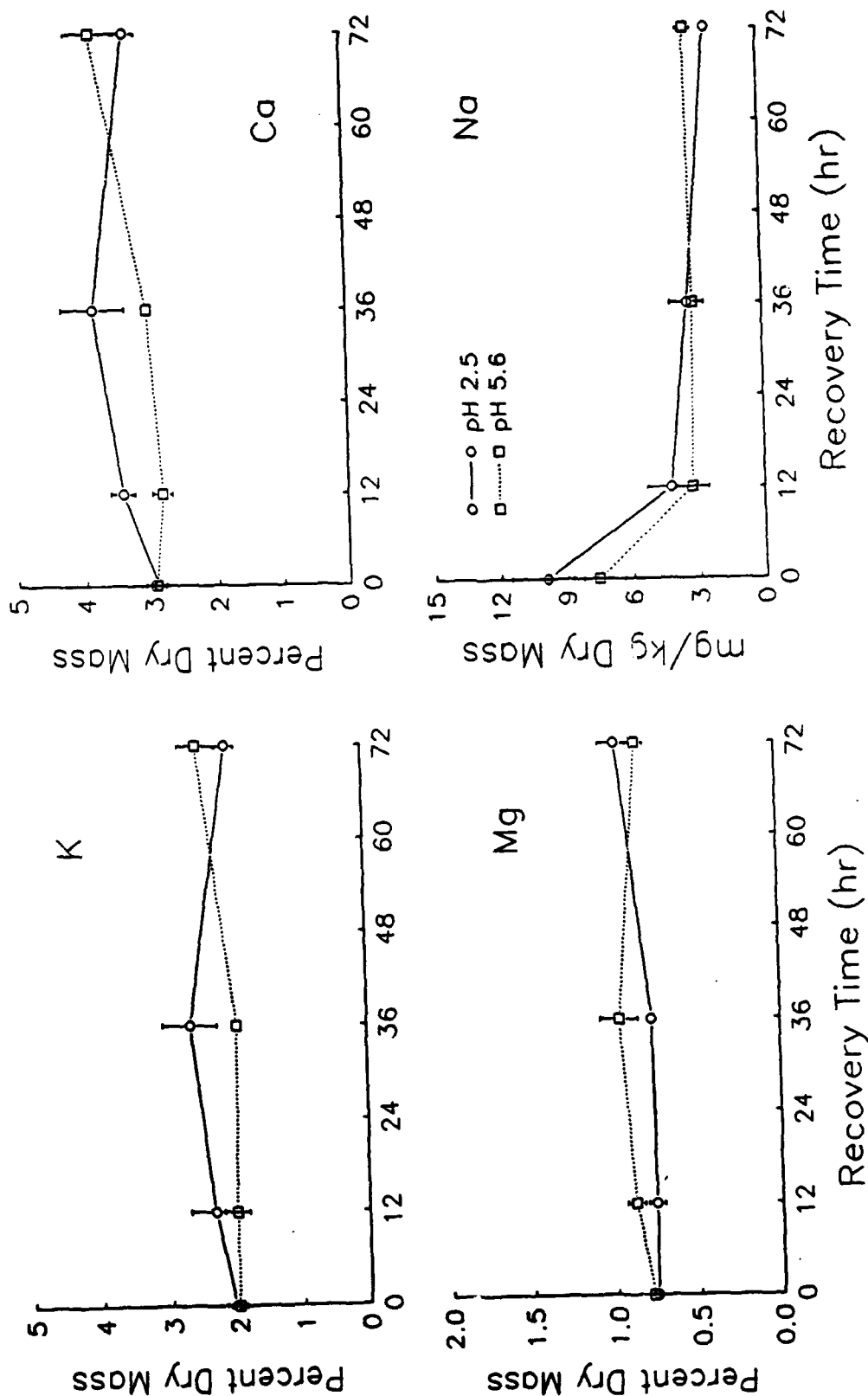
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Figure 6. Mean (± 1 standard error) concentrations of potassium, calcium, magnesium, and sodium in leaves of pinto beans exposed for four hours to mists acidified with HCl. Leaves were sampled immediately after the misting ended (O hr recovery time), and 112, 36, and 72 hours later.

across cell membranes between the leaf symplast and leaf surface moisture was yet another mechanism which could have added cations to droplets. Differences on foliar element concentrations between immediate and 72-hr collections did not provide strong evidence for leaves being able to recover from ion efflux by retranslocation from other tissues or by root uptake (Table 23). However, the dramatic jump in K^+, Ca^{2+}, and Mg^{2+} droplet concentrations between the end of the second misting and the start of the third misting, and the fact that droplet concentrations sometimes increased between the 2- and 4-hr collections, suggested that some leaf element recovery did occur (Fig. 23). However, we cannot explain the apparent lack of recovery between the first and second days.

Since source of acidity did not influence either droplet ion concentrations or to leaf element concentrations, we concluded that it was acidity per se which affected ion efflux rates, with no effect of the associated anions (Cl^- from HCl; SO_4^{2-} and NO_3^- from $H_2SO_4 + HNO_3$).

There was no evidence from the final experiment for any changes in leaf element concentrations (Fig. 6). Therefore, we concluded that, in pinto bean, no short-term replacement of foliar nutrients effluxing into acid surface moisture occurred.

INFLUENCE OF PH AND PLANT NUTRIENT STATUS ON ION FLUXES BETWEEN TOMATO PLANTS AND SIMULATED ACID MISTS

Introduction

As discussed in the BACKGROUND section, two primary mechanisms probably account for most ion efflux and influx between leaves and surface moisture: ion exchange and diffusion along concentration gradients. Our experiments with pinto beans showed that ion enrichment of droplets on leaves was pH-dependent, implying ion exchange (Table 21). Except for Mecklenburg et al.'s (1966) and Blanpied's (1979) experiments, which implicated both ion exchange and diffusion, no available data bear directly on the question of ion diffusion. Experimental manipulation of foliar nutrient concentrations is one way to look at the importance of diffusion, since, if diffusion occurs, ion efflux rates should increase (or influx rates decrease) as foliar ion concentrations increase.

Our final laboratory experiment directly examined the influence of plant nutrient status on whole-plant ion efflux and influx. We had three hypotheses: (1) if ion exchange is occurring, ion efflux rates into acidic moisture on leaves should increase as pH decreases; (2) if ion diffusion is occurring, ion efflux rates at a given pH should increase as foliar element concentrations increase; and (3) if ion exchange and diffusion deplete foliar element pools, ion efflux rates should decrease over time during exposure to acid surface moisture.

Methods.

Plant Culture. Dwarf tomatoes (*Lycopersicon spp.*, Pixie Hybrid II) were grown in hydroponic solutions in order to vary their foliar nutrient concentrations. This species was chosen for two reasons: (1) dwarf plants could readily support the weight of water droplets after several hours of misting without stem reinforcement,

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and (2) they are commercially grown in hydroponic nurseries. Pinto beans, being legumes and requiring root nodulization, were not suited for water culture.

Plants were germinated in sand in shallow trays and watered every two days with a nutrient solution containing ions in proportions (dry mass basis) similar to those shown to produce maximum growth rates in hydroponically grown seedlings of a variety of forest and crop species (Ingestad 1982a, 1987). A concentrated stock solution (Ingestad 1971), diluted 1000-fold, was used to prepare the growth solutions (Table 24).

After two weeks, the seedlings were lifted from the trays and their roots rinsed free of sand with distilled water. They were transferred randomly to one of three 7.6-cm deep, 65-L capacity, rectangular growth tanks constructed of Plexiglass. The tank lids had 32 holes per tank and were painted black to exclude light. Each seedling was held in place in one of the holes by a rubber cork with a hole in its center.

At the start of the hydroponic growth period, each tank was filled to the brim with distilled, deionized water. Stock nutrient solution was added to the tanks daily at relative addition rates (R_a) of 7%, 12%, and 15% d^{-1} (Ingestad 1982b). The formula for calculating amounts to be added was:

$$N_t = N_i \exp (R_a - 1)$$

where N_t = amount of element added on day t and N_i = initial amount of element in all of the plants in a tank. N_i was calculated for potassium, assuming a mean seedling concentration of 4% dry mass (a typical value for fertilized crops; Ingestad and Stoy 1982), a mean seedling dry mass of 0.03 g (determined from fresh-to-dry mass conversion factors for tomato seedlings), and 32 seedlings per tank. Because the stock solution contained elements in constant proportions, adding enough stock to supply the seedlings' need for potassium at a given R_a automatically brought the supply of other elements into line with the same R_a. Ingestad (1982b) showed, in a series of experiments, that after an initial adjustment period of 1-2 weeks, seedling foliar element concentrations stabilized at constant values which were larger at greater R_a.

Twice per week, the pH of the water in each tank, which was initially about 6.2, was checked. If pH fell below 4.0 due to H^+ excretion by roots, sufficient NaOH was added to bring the pH back up to 5.5. Thus, foliar Na concentrations were expected to vary over time and between tanks in a fashion unrelated to R_a. Transpiration gradually reduced the volume of water in each tank, but not enough that water had to be added to any tank to keep the roots submersed.

The tanks occupied a walk-in growth chamber with 16 hr light/8 hr dark photoperiod, 25°C day/20°C night, 450 μmol m^{-2} s^{-1} photosynthetically active radiation at plant height, and high humidity (above 60%).

Plants from each treatment were grown to approximately the same developmental stage, as indicated by numbers of fully expanded leaves. This was 41 days for R_a = 7%, 30 days for R_a = 12%, and 26 days for R_a = 17% because of large differences in growth rates. At this time, the plants were removed from the tanks and the roots of each plant were placed separately in distilled, deionized water in dark glass bottles that were sealed with rubber corks. Samples of the tank water were removed for analysis of ion

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Table 24. Composition of stock nutrient solution, including the relative proportions of elements to nitrogen.

Element	Concentration (g L^{-1})	Proportion
N	25.015	100
K	16.283	65
P	3.255	13
S	2.405	9.6
Ca	1.747	7.0
Mg	2.131	8.5
Fe	0.349	0.7
Mn	0.1005	0.4
B	0.0498	0.2
Cu	0.00756	0.03
Zn	0.00727	0.03
Cl	0.00844	0.034
Mo	0.00163	0.0065
Na	0.00078	0.003

concentrations, and tank water volumes were measured.

<u>Misting Treatments</u>. Each bottle was thoroughly rinsed with distilled, deionized water, then wrapped in thin plastic (Saran wrap). Rubber bands bunched the plastic tightly around the base of each stem above its cork. This procedure allowed "leachate" from mistings to flow down the sides of the bottles without beingchemically contaminated. The foliage of each plant was gathered in gently, using plastic bird netting to prevent contact between foliage of adjacent plants during misting. All plastic items were shown to be chemically clean and, as an additional precaution, were soaked in distilled, deionized water prior to use.

Each plant was subjected to 4 hr of misting at pH 2.5, 4.0, or 5.6 in the same misting chambers with rotating turntables as were used as in the previous experiments with pinto beans. Distilled, deionized water was acidified to the desired pH using HCl. Individual, whole-plant leachates were collected in plastic basins underneath each bottle. There were four plants in each chamber, plus an extra plastic basin to collect non-leachate mist. The 32 plants from each R_a treatment were randomly assigned to receive pH 2.5, 4.0, or 5.6 mist, or to be left unmisted as controls 8 plants per treatment. Plants were randomly allocated to chambers and, because only 12 plants could be misted at a time, were also randomly allocated to receive misting in the morning or the afternoon.

Leachate samples were collected at 15, 30, 60, 120, and 240 min after the start of misting, during which the nozzles were temporarily turned off. An aliquot of each sample was poured into a plastic bottle for storage in the dark at $4^\circ C$. The remainder of each sample was weighed and discarded.

At the end of each misting day, the plants were allowed to dry. The next day, each plant was separated into leaves, stems plus petioles, and roots. All the leaflets were removed from two plants in each treatment/chamber combination (random selection of plant and leaf position on stem) and their one-sided surface areas measured with a digital planimeter. Then the samples were oven-dried, weighed to ±0.001 g, and stored in coin envelopes. Total leaf area per plant was calculated by multiplying the specific leaf areas ($cm^2\ g^{-1}$) of the leaves subsampled for area by total leaf mass.

Aqueous samples were analyzed for pH, cations (K^+, Ca^{2+}, Mg^{2+}, Na^+) and anions (SO_4^{2-}, NO_3^-, PO_4^{3-}). Chloride was not analyzed because HCl was used to acidify the mists. Plastic gloves were worn at all times for sample handling to prevent chemical contamination.

<u>Statistical Analyses</u>. The ion concentrations in the non-leachate samples from each chamber on each day were subtracted from the corresponding plant leachate ion concentrations to correct for background chemical contamination. Ion influx/efflux rates were expressed on a unit leaf surface area and unit time basis ($meq\ m^{-2}\ h^{-1}$) to normalize for differences in leaf area between plants and differences in time elapsed between successive collections of leachate. Repeated-measures ANOVA was used to test for the significance of between-subjects effects (R_a or "nutrient" and mist acidity or "pH" factors) and within-subjects effects (time of collection within nutrients or pH), using SYSTAT software (Wilkinson 1984).

Results.

Plant Growth. Plants from the R_a = 7% and 17% d^{-1} tanks were of similar size, while plants from the R_a = 12% d^{-1} tank were somewhat larger (Table 25). Mean leaf area per plant and the fraction of total plant mass allocated to foliage were similar for R_a = 12% and 17% d^{-1} plants, but were significantly less for R_a = 7% d^{-1} plants (Table 25).

Plant Nutrient Uptake and Concentrations. Total plant uptake of elements from each tank was calculated by subtracting the total amount of each element remaining in the tank when the plants were removed from the cumulative amount added, in the stock solution. The greater the R_a, i.e., the larger the amount of each element added to each tank, the greater the amount of each element absorbed by the plants (Table 26). At R_a = 7% and 12% d^{-1}, nutrient uptake was nearly or entirely quantitative (79-100% of supply absorbed) for all elements except Na. At R_a = 17% d^{-1}, a smaller proportion of each added element was absorbed, suggesting that the maximum relative growth rate for the tomato plants was less than 17% d^{-1} (Table 26).

We divided the total mass of elements absorbed from each tank by the total dry mass of the plants in that tank to calculate mean plant element concentrations for each R_a treatment. For all elements except Na, which was not added in proportion to the other elements because of NaOH additions to maintain pH, plant concentrations increased with increasing R_a (Table 27). With the exception of K at R_a = 17% d^{-1} and Na at all values of R_a, the proportions of elements in the plants were similar to those in the stock nutrient solution (compare Tables 24 and 27). Thus, our objective of comparing plants with different nutrient status was fulfilled.

Leachate Neutralization. In general, contact of the misting solutions with the tomato plants resulted in acidification of pH 5.6 mists, neutralization of pH 2.5 mists, and little change in the acidity of pH 4.0 mists (Table 28). There was no relationship between the amount of neutralization and either R_a or time of collection (ANOVA, P > .05; Table 29).

Ion Efflux/Influx Rates. Plant nutrient status exerted a significant (ANOVA, P < 0.05) effect on the flux rates of all ions from foliage into leachate, while mist pH was a significant influence on flux rates of all ions except SO_4^{2-} (Table 29). Leachate pH was not affected by nutrient status and was strongly affected by intial mist pH. The latter result is hardly surprising, given the small amount of mist neutralization (Table 28). Time of collection was a significant factor affecting most ion flux rates, both within nutrient status (all pH values combined) and within mist pH (all R_a values combined; Table 29). However, mist pH did not change with time. Ion flux rates behaved in three general ways, depending on the ion. In the case of K^+, Mg^{2+}, NO_3^-, and PO_4^{3-}, flux rates within each R_a treatment were low and constant over time at pH 5.6 and 4.0, but increased over time at pH 2.5 (Figs. 7 and 9). The higher the R_a, the greater the time-dependent rate of increase at pH 2.5.

Table 25. Mean values per plant of various growth parameters in relation to relative nutrient addition rate.

R_a (% d^{-1})	Leaf Area (cm^2)	Leaf Mass (g)	Stem Mass (g)	Root Mass (g)	Total Mass (g)
7	434	0.32	0.24	0.28	0.83
12	949	0.45	0.26	0.27	0.98
17	1000	0.39	0.20	0.22	0.81

Table 26. Amount of elements (mg) added to growth tanks and absorbed by the plants growing in each tank.

Element	$R_a = 7$% d^{-1}			$R_a = 12$% d^{-1}			$R_a = 17$% d^{-1}		
	added	absorbed	% abs	added	absorbed	% abs	added	absorbed	% abs
N	1057	1037	98	2686	2518	94	4843	2878	59
K	688	652	95	1749	1718	98	3152	2314	73
P	138	133	96	350	350	100	630	464	74
S	102	89	87	258	232	90	466	269	58
Ca	74	71	96	188	148	79	338	210	62
Mg	90	86	96	229	204	89	413	237	57
Na*	79	63	80	127	66	52	59	14	24

*Includes NaOH additions.

Table 28. Neutralization (change in pH) of applied acid mist solutions.

Mist pH	Time (minutes)				
	15	30	60	120	240
$R_a = 7\%\ d^{-1}$					
2.5	0.06	0.00	0.06	0.06	0.06
4.0	-0.04	0.00	-0.01	0.02	0.02
5.6	-0.40	-0.56	-0.41	-0.26	-0.25
$R_a = 12\%\ d^{-1}$					
2.5	0.04	0.06	0.05	0.04	0.04
4.0	0.04	0.00	0.01	0.00	0.02
5.6	-0.23	-0.04	-0.14	-0.13	-0.16
$R_a = 17\%\ d^{-1}$					
2.5	0.04	0.04	0.02	0.02	0.01
4.0	-0.02	0.00	-0.02	-0.02	-0.01
5.6	-0.07	-0.17	-0.20	-0.19	-0.10

Table 27. Mean concentration (% dry mass) of elements in plant tissues, and their relative proportions in nitrogen.

Element	$R_a = 7\%\ d^{-1}$		$R_a = 7\%\ d^{-1}$		$R_a = 7\%\ d^{-1}$	
	% Dry Mass	Proportion	% Dry Mass	Proportion	% Dry Mass	Proportion
N	3.92	100	8.00	100	11.09	100
K	2.46	63	5.46	68	8.92	81
P	0.50	13	1.11	14	1.79	16
S	0.34	9	0.74	9	1.04	9
Ca	0.27	7	0.47	7	0.81	7
Mg	0.32	8	0.65	8	0.91	8
Na	0.24	6	0.21	3	0.05	<1

Table 29. Results of repeated-measures analysis of variance for the tomato
          leaching experiment.

Factor	Ion Flux Rate			
	pH	K^+	Ca^{2+}	Mg^{2+}
between subjects				
nutrients	0.21	0.002	0.01	0.007
mist pH	<0.001	<0.001	<0.001	<0.001
nutrients x pH	0.10	<0.001	0.78	<0.001
within subjects				
time in nutrients	0.21	<0.001	0.55	<0.001
time in pH	0.86	<0.001	<0.001	<0.00
	Na^+	SO_4^{2-}	NO_3^-	PO_4^{3-}
between subjects				
nutrients	0.005	0.027	<0.001	<0.001
mist pH	<0.001	0.51	<0.001	<0.001
nutrients x pH	0.24	0.056	<0.001	<0.001
within subjects				
time in nutrients	<0.001	0.043	<0.001	<0.001
time in pH	0.527	0.27	<0.001	<0.001
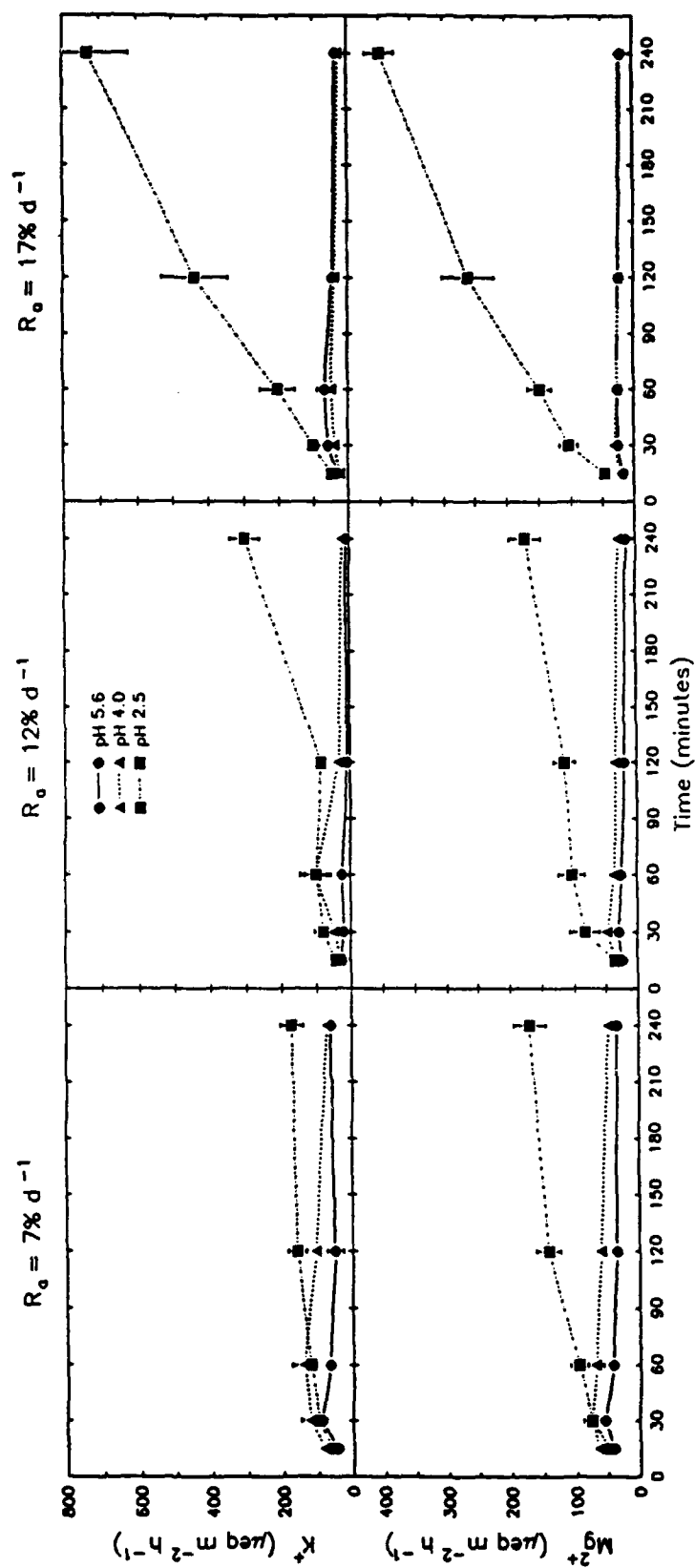
Figure 7. Mean (± 1 standard error) concentrations of potassium and magnesium in whole-plant leachates from tomatoes exposed for four hours to mists acidified with HCl. Tomatoes were supplied hydroponically with nutrients at three relative addition rates prior to mistings. Time is cumulative from the start of each misting.
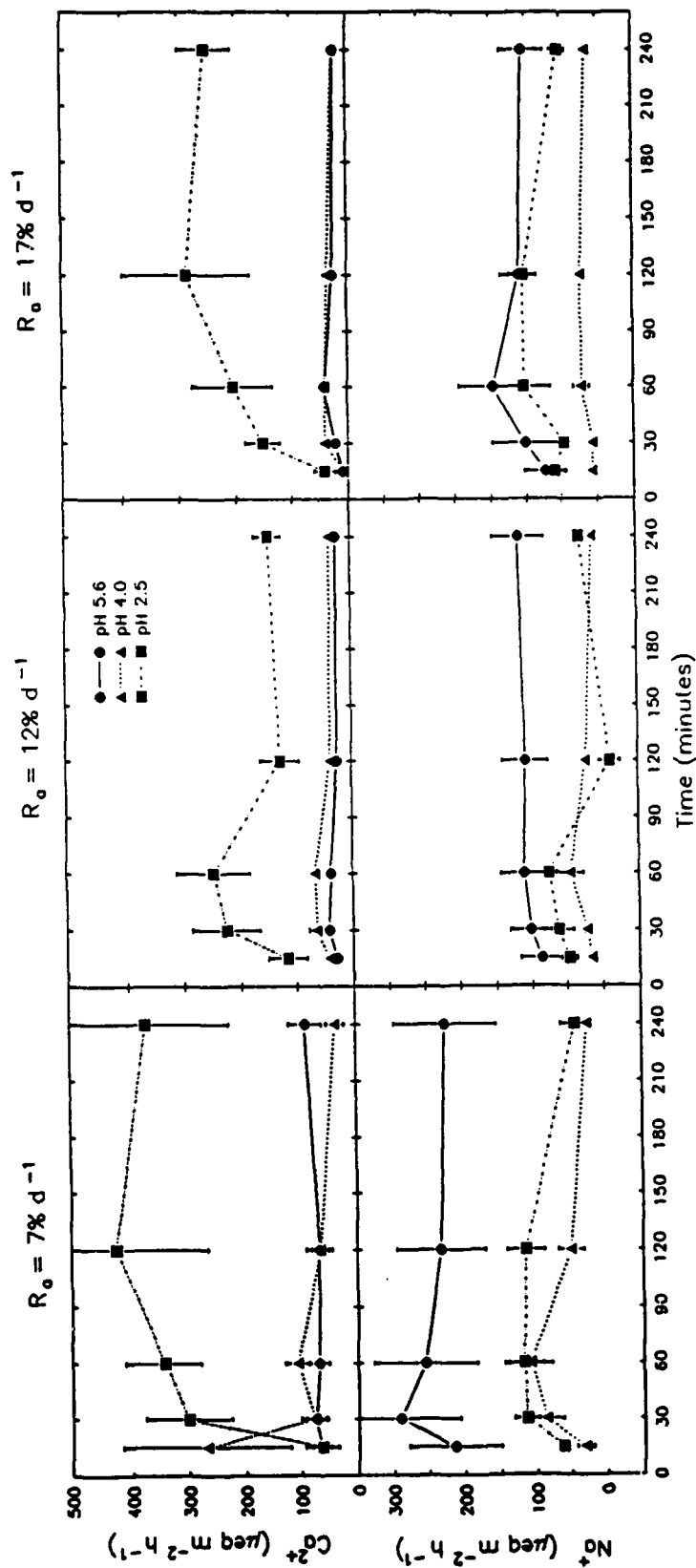
Figure 8. Mean (± 1 standard error) concentrations of calcium and sodium in whole-plant leachates from tomatoes exposed for four hours to mists acidified with HCl. Tomatoes were supplied hydroponically with nutrients at three relative addition rates prior to mistings. Time is cumulative from the start of each misting.
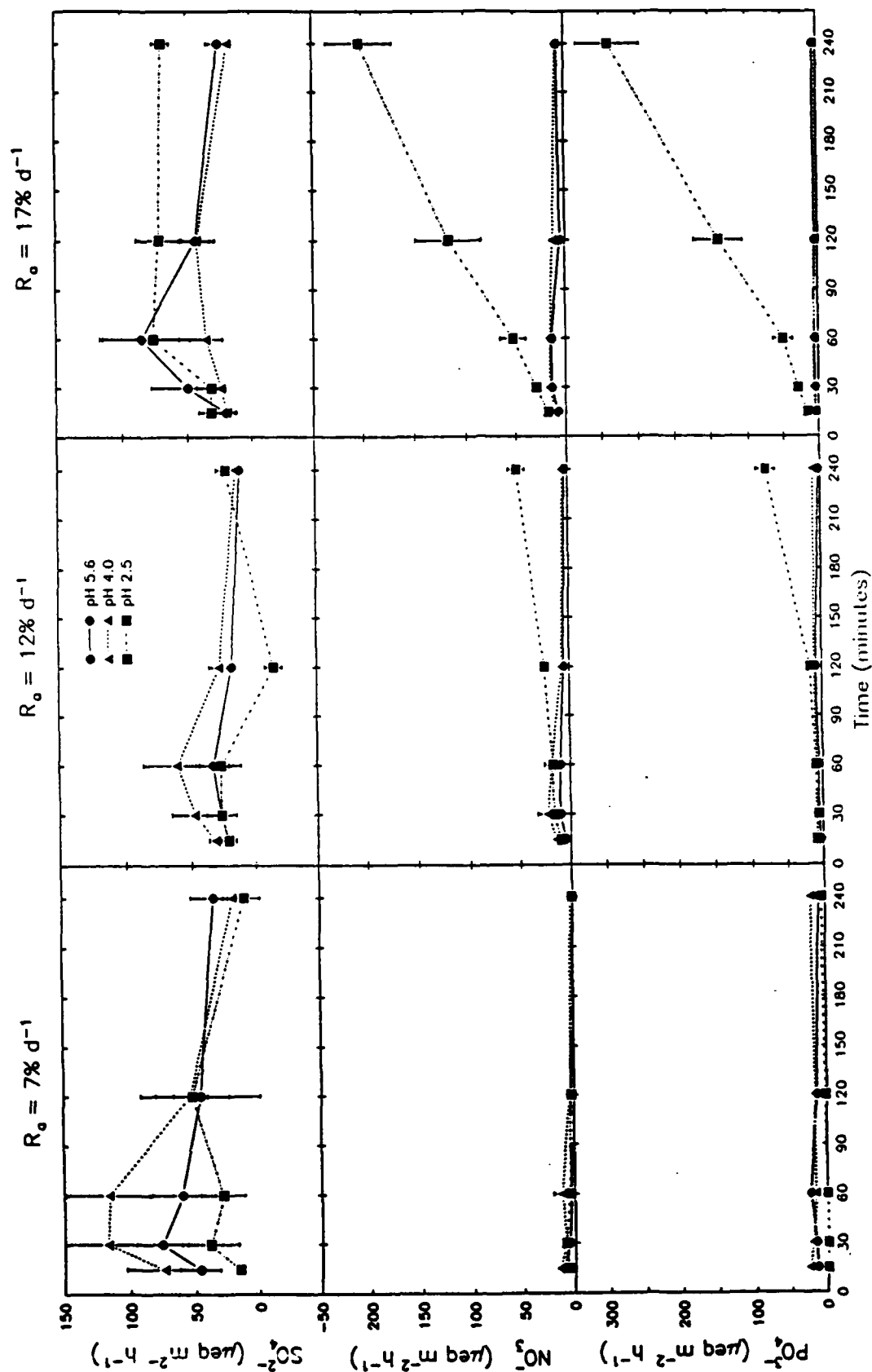
Figure 9. Mean ($\pm$ 1 standard error) concentrations of sulfate, nitrate, and phosphate in whole-plant leachates from tomatoes exposed for four hours to mists acidified with HCl. Tomatoes were supplied hydroponically with nutrients at three relative addition rates prior to mistings. Time is cumulative from the start of each misting.

Calcium flux rates changed little with time at pH 2.5 and 4.0, except for an intial high rate at 15 min at pH 4.0 with R_a = 7% d^{-1} (Fig. 8). At pH 2.5, Ca^{2+} flux rates increased rapidly duirng the first 30-60 min, then remained constant or decreased. Unlike K^+, Mg^{2+}, NO_3^-, and PO_4^{3-}, maximum Ca^{2+} flux rate occurred at R_a = 7% d^{-1}.

The third behavior was exhibited by Na^+ and SO_4^{2-}, whose flux rates showed poor relationships between mist pH and R_a (Figs. 8 and 9). Sodium flux rate was maximum at pH 5.6 for R_a = 7% d^{-1}; these plants had the highest tissue Na concentrations (Table 27).

The time-varying differences between the flux rates of K^+, Mg^{2+}, NO_3^-, and PO_4^{3-} at varying pH, and their dependence on R_a (Figs. 7-9), provided an explanation for the significance of the nutrient x pH interaction for some ions (Table 29).

Discussion

Increasing rates of ion efflux from foliage with decreasing mist pH have been reported for Ca^{2+} with tobacco (Fairfax and Lepp 1975), for K^+, Ca^{2+}, and Mg^{2+} with sugar maple and pinto bean (Wood and Bormann 1975), and for K^+ and Ca^{2+} with yellow birch and white spruce (Scherbatskoy and Klein 1983). However, K^+ efflux decreased with decreasing pH for tobacco, while Mg^{2+} efflux was unaffected by pH in tobacco (Fairfax and Lepp 1975), and Na^+ and NO_3^- efflux were not influenced by pH for birch and spruce (Scherbatskoy and Klein 1983). Haines et al. (1985) found no pH-dependence of NH_4^+, NO_3^-, Ca^{2+}, Mg^{2+}, K^+, or PO_4^{3-} efflux rates from foliage of nine different broadleaf plants.

We suggest that these conflicting results between various experiments may be caused in part by differences in plant foliar nutrient concentrations. If diffusion is one of the mechanisms causing ion efflux or influx, then some attempt must be made to control internal leaf element concentrations. We did just that in our experiment. Of course, the plant pools of elements available for diffusion or ion exchange are some unknown fraction of total elemental content. For relatively "immobile" elements such as Ca, much of the foliar pool is bound up in cell walls, while for a relatively "mobile" element such as K, most of the element is in solution as ions in the apoplast or the cytoplasm. Thus, total foliar pools (mobile + immobile) can provide only a rough guide to the actual ion concentration gradients between leaves and surface moisture. Nevertheless, increasing plant element concentrations should increase the magnitude of these gradients.

To our knowledge, this experiment was the first to consider changes in whole-plant ion leaching over the course of individual acid mist treatments. Successive mistings spaced several days apart (e.g., Scherbatskoy and Klein 1983) suffer from the possible confounding influence of replacement of leached foliar elements by translocation from elsewhere in the plant or by root uptake. Changes in droplet ion concentrations, the emphasis of our previous experiment with pinto beans, can give very misleading indications of whole-plant leaching because whether individual droplets were recently deposited or had been on the foliage for a long time, and the total volume of droplets, were unknown. By collecting all leachate at regular intervals during misting, and by growing plants in clean environments and rinsing their leaves prior to mistings, we minimized contamination by dry deposition. This was clearly demonstrated by

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the generally low initial 15-min flux rates of ions into the leachates, and by the fact that flux rates often increased over time (Figs. 7-9).

How did the patterns of ion flux rates over time from tomatoes compare with flux rates from "natural" foliage in the field? Reiners and Olson (1984) performed time-course studies of ion fluxes from foliated balsam fir shoots into simulated acid rain (pH = 4.1) in outdoor experiments. For K^+, SO_4^{2-}, and NO_3^-, flux rates were intially high, then decreased exponentially over time to rates near zero. These ions exhibited similar temporal patterns (after correction for varying rain rates) in sequential throughfall/stemflow collections during the course of individual rain events in a natural balsam fir forest (Olson et al. 1985). In the shoot experiments, Na^+ showed declining flux rates over time at high rain rates, but lower and time-insensitive flux rates at low rain rates.

The patterns we observed for these ions were quite different. Sulfate and Na^+ flux rates were relatively constant over time at all pH values, while K^+ and NO_3^- flux rates were time-invariant at pH 4.0 and 5.6, but increased rapidly over time at pH 2.5 (Figs. 7-9). Why such sharp differences in the behavior of K^+, SO_4^{2-} and NO_3^- between our experiment and work with balsam fir? We believe that the explanation is provided by pre-existing dry deposition on foliar surfaces, which was undoubtedly present in the balsam fir experiments but was minimized in our experiment.

Did our data provide support for ion exchange and/or ion diffusion? There was clearly a pH effect, but it showed a "threshold" value somewhere between 4.0 and 2.5, because there were seldom any significant differences in flux rates, regardless of time of collection, between pH 4.0 and 5.6, while large differences appeared between pH 2.5 and 4.0 for several ions (Table 29). However, the differences between flux rates of these ions to pH 2.5 vs. pH 4.0/5.6 mists increased over time. If ion exchange was the only mechanism causing ion fluxes, then flux rates should have been either independent of time or should have decreased over time as exchangeable foliar element pools were exhausted. If diffusion was the only mechanism, the same outcomes should have occurred, depending on whether or not ion efflux rates were sufficient to deplete pools of dissolved ions in foliage.

A possible explanation for this unusual behavior was direct damage to the leaf surfaces by the pH 2.5 mists. As pH 2.5 mist droplets dried following each experiment, small, pale green lesions appeared on the leaves of all plants. Fewer lesions appeared on plants from the $R_a = 7\%$ d^{-1} treatment than in the other treatments. Lesions involve cuticle erosion and membrane degradation, and thus may be sites for enhanced ion fluxes between surface moisture and leaf interiors. Although not visible during misting, lesions may have been forming progressively as the mistings proceeded, providing a pathway for efflux of ions. However, this explanation did not in itself distinguish between ion exchange and diffusion.

The enhanced rate of increase in flux rates at pH 2.5 for K^+, Mg^{2+}, NO_3^-, and PO_4^{3-} as R_a increased suggested that diffusion was occurring, i.e., the leaf-to-surface moisture ion concentration gradient was increased because of higher concentrations of dissolved ions in the leaf apoplast.

SUMMARY

We undertook field measurements and laboratory studies to determine to what extent, and by what mechanisms, acidic emissions from space shuttle launches in fog- and dew-forming environments, or exposure of plants to ambient acid wet deposition, could affect plant nutrient status. Detailed field studies were carried out on the role of rain, fog, and dew in scavenging aerosols and gaseous pollutants from the atmosphere, transferring these chemicals to plant surfaces, and exchanging them with leaf interiors. Complementary laboratory experiments compared the effects of solution pH, source of acidity (HCl from shuttle launches vs. sulfuric/nitric acids in ambient acid rain), duration of wetting events, single vs. multiple wetting events, and plant nutrient status on ion exchanges between leaves and surface moisture. Both the field and the lab studies asked the question whether or not exposure to acid wet deposition alters internal foliar element concentrations.

The results of the field studies suggested that in a frequent fog- and dew-forming environment such as Vandenberg Air Force Base, acidic emission products from shuttle launches could be efficiently transferred by fogs and dews to plant surfaces. Despite our sampling site's location within a region where acid aerosols and pollutant gases have lowered rain pH to around 4.3 and fog pH to even lower values, dew, contrasting strikingly to fog, does not appear to function as a prime mechanism for depositing acidic atmospheric substances to leaf surfaces. However, dew can solubilize acidic materials already present on leaf surfaces.

When we measured rain, fog, and dew at the same location in urban Indianapolis, pH decreased in the order dew > rain > fog. Rain pH showed week-to-week variation between 3.77 and 5.13, with a volume-weighted mean of 4.30. The source of the acidity, as with acid rain elsewhere in Indiana, was absorbed SO_2, NO_2, and HNO_3 gases and rain droplet scavenging of sulfate and nitrate aerosols, since SO_4^{2-} and NO_3^- were the dominant anions in rain. The presence of NH and Ca in rain implied scavenging of carbonate aerosols originating from the surrounding, predominantly agricultural landscape, causing partial neutralization of rain acidity. Rain chemistry in Indianapolis was very similar to surrounding regions, suggesting that it represented regional, rather than local, atmospheric chemistry.

Fog pH varied between 2.9 to 4.1, and, as with rain, the dominant anions were SO_4^{2-} and NO_3^-, and NH_4^+ and Ca^{2+} were the major cations. The much lower pH of fog compared to rain reflected the fact that it scavenged local pollutants, which included high concentrations of acid gases and aerosols in our urban environment, and the lesser dilution in small fog droplets compared to large raindrops.

Dew pH ranged from 6.1 to 7.2, even though SO_4^{2-} and NO_3^- were still present at substantial concentrations. Bicarbonate (HCO_3^-) was the dominant anion and there were high concentrations of Ca^{2+}, suggesting that sedimenting carbonate dust concurrent with dew formation neutralized much of the acidity generated by pollutant gas absorption. The source of this dust was probably agricultural lands with calcareous soils surrounding Indianapolis. Individual dews also showed dynamic changes in pH and ion concentrations over the course of the night, reflecting the fact that dew forms initially as deionized water,

then subsequently scavenges pollutants. We conclude that dew and fog chemistry more accurately reflect local atmospheric chemistry than does rain.

Our field studies also showed that vegetation exchanges chemical constituents with the atmosphere by a number of mechanisms, some of which are active simultaneously, depending on whether rain, dew, fog, or dry conditions prevail. The form of wet deposition (rain vs. dew) involved, the duration of rain/dew events and preceding dry weather, the amount of dry-deposited aerosols on leaf surfaces, and the direction and magnitude of ion fluxes between leaf surface moisture and leaf interiors were primary factors in determining the dynamics of chemical exchange.

Measurements of aerosol deposition to chemically inert collectors and leaves during rainless periods showed that amounts of dry deposition on inert collectors were generally positively correlated with the number of hours of dry exposure. However, aerosol deposition to foliage often was not significantly correlated or was even negatively correlated with length of the dry period. Our two test species, sugar maple and flowering dogwood, apparently differed in their collection (or retention) efficiencies for aerosols, though not uniformly across all ions. Accumulation of aerosols on leaves did not generally differ from accumulation on inert surfaces, although nitrate, a major nutrient, was apparently absorbed by dogwood leaves.

Significant chemical exchange occurred between acid surface moisture and foliage, as shown by partial neutralization (increased pH) of rain and dew droplets on leaf surfaces, and by increased or decreased ion concentrations in leaf surface moisture compared to ambient rain and dew. In general, there was efflux of K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and NO_3^- from leaves into rain and dew, but influx of NH. These results were consistent with previous studies of forest throughfall and of acid mist leaching in controlled environments.

The mechanisms of chemical exchange between leaves and surface moisture probably included ion exchange (H^+ for cations) and ion diffusion along concentration gradients between surface moisture and leaf apoplasts, although our data could not distinguish between these two possibilities.

Hardwood saplings exposed to ambient acid rain and dew did not display measurable changes in foliar element (K, Ca, Mg, Na) concentrations as a result of individual or multiple rain/dew events. Since several ions showed net efflux out of leaves into surface moisture, this result suggested that one or more mechanisms compensated for nutrients leached from foliage. First, lost nutrients may have been replaced rapidly either by root uptake or by translocation from other, non-leaf pools. Second, nutrient fluxes out of foliage might have been small compared to foliar nutrient pool sizes, and therefore were obscured by the natural variability in pool sizes among leaves and saplings.

Because leaf surface droplet chemistry is strongly influenced by preexisting surface contamination, plant species that "capture" aerosols efficiently may be exposed to higher concentrations of chemicals in surface droplets, particularly as they evaporate, than in ambient rain, fog, and, dew. This effect is most pronounced for dew, which forms initially as pure water. Therefore, in considering mechanisms of scavenging and deposition of acid substances from the atmosphere, the dominating influence of aerosol

deposition on plant surfaces, and the tendency of plants to neutralize droplets of rain, dew, and fog, must be noted. In heavily industrial and non-agricultural areas, or near strong point sources, of course, this generalization may not hold. Clearly, however, in estimating plant dose-response effects, the composition and acidity of aqueous solutions in direct contact with leaf surfaces, rather than just atmospheric concentrations or chemical composition on chemically clean and inert surfaces, must be known.

Given the presence of highly acid fogs in Indianapolis, and the potential for them to occur at Vandenberg AFB following shuttle launches, experiments were conducted to determine whether or not acid mists promote substantial nutrient losses from leaves.

Both HCl and sulfuric/nitric acids were used as sources of acidity to produce simulated mists of various pH. The first is the principal acid in shuttle emissions and the latter are dominant acids in air pollution across most of the United States. Applying HCl-acidified mists over a range of pH from 1.0 to 5.6 onto leaves of the common beet suggested that effects depended on the ion in question, but that measurable reduction of foliar element concentrations occurred only when the mist acid was concentrated enough to kill the leaves under our experimental conditions. This outcome was repeated even when several sequential mistings were carried out. Mists of pH 1.0 caused greater efflux of ions out of leaves into leaf surface droplets than did mists of higher pH, but little difference was seen between droplet ion concentrations at pH 2 and those in less acid treatments.

Because nutrient efflux from beet leaves into HCl-acidified mists was limited largely to the extremely acid pH 1.0, it was logical to ask whether in a more sensitive plant, such as pinto bean, acids formed from $H_2SO_4 + HNO_3$ would affect ion losses at lower acidities than those formed from HCl. H_2SO_4 and HNO_3 were mixed in a 2:1 ratio, similar to ambient rainfall in the eastern U.S. Experimental acidities of 2.5 and 4.0 typified the most acid fogs observed and the lower limit of ambient rainfall, respectively.

Visible leaf injury in pinto bean occurred at pH 2.5 within 24 hr of treatment with both HCl and $H_2SO_4 + HNO_3$ mists, revealing beans' greater tendency than beets to form lesions. However, in terms of ion efflux from foliage into leaf surface droplets, the two species responded similarly to acid misting. Furthermore, the $H_2SO_4 + HNO_3$ mists did not elicit a significantly different effect than did the HCl mists. The only apparent effect on foliar element concentrations was a reduction as pH 2.5 misting was repeated on successive days, underscoring the inadequacy of single treatments for determining acid wet deposition effects.

Our results did not clearly indicate by what mechanisms changes in droplet chemical composition occurred after contact with leaf surfaces. There may have been some solubilization of surface aerosols, but the effect appeared minor. The same conclusion applied to active (energy requiring) absorption or excretion by the leaves. Similarly, diffusion of ions between leaf apoplasts and droplets was assumed to be taking place, but since cation concentrations changed erratically and unpredictably over the course of the experiment, diffusion appeared not to be a consistent mechanism. Exchange involving H^+ and other cations adsorbed to the leaf epidermis or held within the apoplast also was a potential explanation for the higher droplet cation concentrations in pH 2.5 mist treatments, but the lack of difference in ion

concentrations between pH 4.0 and 5.6 mists suggested that ion exchange was unimportant at high pH.

To shed more light on the question of the relative importance of ion exchange vs. ion diffusion in explaining ion fluxes between leaves and surface moisture, we exposed tomatoes for 4 hr to mists acidified with HCl. Three sets of plants were grown hydroponically at three levels of nutrient availability, resulting in higher tissue element concentrations as nutrient supply increased. Plants were grown in clean growth chambers and foliage prerinsed to remove aerosol contamination.

At a mist pH of 5.6 and 4.0, most ions showed small efflux rates from foliage and the rates did not change over the course of the mistings or in response to plant nutrient status. However, efflux rates of K^+, Ca^{2+}, SO_4^{2-}, and NO_3^- increased dramatically with time as mistings proceeded, and the rates of increase were greater as plant element concentrations increased. These results suggested that both ion exchange, as indicated by the pH effect on efflux rates, and ion diffusion, as shown by the nutrient status effect on efflux rates, were operating. There also appeared to be a "threshold" pH value below which ion effluxes increased substantially.

We conclude that fog and dew are efficient scavenging media for locally-generated acidic substances and other pollutants in the atmosphere, and can transfer substantial quantities of these materials to nearby vegetation. Preexisting surface contamination or concurrent aerosol deposition can significantly alter the chemistry of leaf surface water droplets. In addition, ion fluxes between leaf tissues and surface moisture can partially neutralize droplet acidity and enrich or deplete droplet ion concentrations relative to ambient rain, fog, and dew.

There was no evidence for nutrient depletion in the foliage of plants exposed to acid wet deposition in the field or the laboratory. However, it would be premature to conclude that this does not occur in nature, since we could not exert control over plant nutritional status in the field studies.

We hypothesize that plants growing on nutrient-rich soils, as in fertilized agricultural fields, may experience higher loss rates of ions into acid surface moisture than plants growing on nutrient-poor soils. However, plants on infertile soils, such as the sand dunes at Kennedy Space Center and Vandenberg AFB, may suffer depletion of foliar nutrient pools because of the small initial pool sizes and low soil nutrient concentrations. Whether or not this occurs will depend on the balance between whole-plant nutrient losses and whole-plant nutrient uptake over the course of repeated exposures to acid wet deposition. In the case of extremely acid fogs and dews, as might occur following shuttle launches at Vandenberg AFB, direct visual injury to nearby vegetation could cause rapid nutrient losses independent of plant nutrient status.

Additional laboratory misting experiments, where plant nutrition and mist pH can be closely regulated, in combination with field studies of plants growing on fertile and impoverished soils, will be needed to critically test these hypotheses. These studies will require use of whole-plant element mass balance equations, and the need to control for the influence of previous aerosol deposition will tax the ingenuity of the investigators. Only by addressing these difficulties, however, can we hope to definitively answer the disarmingly simple question, "Does acid deposition cause losses of nutrients from plants?"

PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS

Muir, P.S., K.A. Wade, B.H. Carter, T.V. Armentano, and R.A. Pribush. 1986. Fog chemistry at an urban midwestern site. *Journal of the Air Pollution Control Association* 36:1359-1361.

See Appendix A of this report.

Muir, P.S. 1988. Acid mist-induced leaching of foliar cations: the influence of pH and source of acidity. Submitted to *Water, Air, and Soil Pollution.*

Pinto bean plants were misted on three separate occasions using pH 2.5 and 4.0 water acidified with HCl or a combination of H_2SO_4 and HNO_3, and with deionized water (pH 5.6). Concentrations of K^+, Ca^{2+}, and Mg^{2+} in water droplets on leaf surfaces were positively correlated with mist pH, but were not influenced by source of acidity. Droplet pH and cation concentrations generally increased during successive mistings at a mist pH of 2.5, but decreased or remained constant at mist pH of 4.0 or 5.6. The temporal pattern of droplet ion concentrations within each misting event was different for each cation/pH treatment combination. Elemental analysis of leaves showed no evidence for depletion of foliar elements in response to ion efflux into acid surface moisture.

Foster, J.R., and R.A. Pribush. The chemistry of dews in an urban environment. In preparation for *Atmospheric Environment.*

Dews and frosts formed on a chemically inert Teflon surface were sampled for pH and ion concentrations during a 15-month period in Indianapolis, Indiana. Despite earlier predictions in the literature that dews should be acid due to absorption of sulfur dioxide, nitrogen dioxide, and nitric acid gases, measured pH ranged from 6.0 to 7.2. The dominant anions were sulfate, nitrate, and bicarbonate, while ammonium and calcium were the dominant cations. High concentrations of bicarbonate, and a consistent presence of calcium, sodium, and magnesium ions lacking gaseous sources, implied that sedimentation of atmospheric aerosols occurred during dew formation and resulted in neutralization of dew acidity. Temporal sampling of indiviudal dews at two locations showed that dew chemistry changed substantially during the course of the night and was influenced by local atmospheric chemistry.

Foster, J.R. The influence of pH and plant nutrient status on ion fluxes between tomato plants and simulated acid mists. In preparation for *New Phytologist.*

Plant foliage is known to interact chemically with acidic surface moisture by the mechanisms of ion exchange and ion diffusion. Although it has been hypothesized that ion efflux into acid moisture could deplete foliar nutrient pools, this has yet to be unequivocally demonstrated in the field or laboratory. We grew tomato plants hydroponically, using three relative addition rates (7%, 12%, and 15% per day) for nutrients in constant proportions. Plants at higher addition rates grew faster and had greater tissue element concentrations. At the same stage of development, plants at each addition rate were exposed to simulated acid mists of pH 2.5, 4.0, or 5.6, using HCl as the source of acidity, or left unmisted as controls. Aerosol contamination on leaf surfaces was excluded by prerinsing leaves. Efflux rates of most ions from leaves into whole-plant leachates were small and showed little change over the course of 4-hr mistings at pH 5.6 and 4.0. However, at pH 2.5, efflux rates of K^+, Mg^{2+}, SO_4^{2-}, and NO_3^- increased over time, with faster rates of increase as plant nutrient status increased. These results suggested that (1) very acid wet deposition is required to cause substantial ion efflux from leaves, and that (2) ion efflux rates may be greatest for plants growing on nutrient-rich soils.

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Pribush, R.A., B.H. Carter, and J.L Waugh. Acid precipitation in urban and rural Indianapolis. In preparation for *Journal of the Air Pollution Control Association.*

Since July 1985, wet and dry deposition samples have been collected weekly in Indianapolis, IN, and analyzed using the protocols of the National Acid Deposition Program (NADP). Measured pH varied between 3.77 and 5.13, with a volume-weighted mean of 4.30. Annual mean pH varied only 0.01 units from 1986 to 1988. Rainfall with highest acidity was observed in summer and winter. Sulfate concentration was maximum in August, while nitrate concentration was maximum in January. Calcium concentration was highest in early spring; ammonium ion concentration peaked in winter. Indianapolis annual mean pH and ion concentrations were in excellent agreement with those shown on NADP annual isopleth maps, for which it can be inferred that there was not an obvious influence of urban Indianapolis compared to the all-rural NADP sites. However, relative to surrounding rural NADP sites, Indianapolis rain had lower concentrations of acid-producing sulfate and nitrates, and much lower concentrations of neutralizing calcium and ammonium concentrations. As a result, Indianapolis rain pH was slightly lower than those of surrounding stations.

PRESENTATIONS AT SCIENTIFIC MEETINGS

Foster, J.R., R.A. Pribush, and B.H. Carter. 1988. The chemistry of dew in an urban environment. Paper presented at Ecological Society of America annual meeting, University of California, Davis, CA.

Muir, P.S. 1988. Acid mist-induced leaching of foliar cations: the influence of pH and source of acidity. Paper presented at American Association for the Advancement of Science, Pacific Division, annual meeting, Oregon State University, Corvallis, OR.

Pribush, R.A., and B.H. Carter. 1988. A comparison of rain, dew, and fog as atmospheric scavenging media in an urban environment. Paper presented at American Chemical Society, Division of Environmental Chemistry, annual meeting, Toronto, Canada.

GRANT PROPOSAL

Foster, J.R., and R.A. Pribush. 1988. Factors controlling chemical deposition to vegetation by dew. Exploratory Research Grants Program, Environmental Air/Water Chemistry and Physics Program, U.S. Environmental Protection Agency.

LITERATURE CITED

Adams, C.M., and T.C. Hutchinson. 1984. A comparison of the ability of leaf surfaces of three species to neutralize acidic rain drops. *New Phytologist* 97:464-478.

Adams, C.M. and T.C. Hutchinson. 1987. Comparative abilities of leaf surfaces to neutralize acidic raindrops. II. The influence of leaf wettability, leaf age and rain duration on changes in droplet pH and chemistry on leaf surface. *New Phytologist* 106:437-456.

Alkezweeny, A.J., and K.M. Busness. 1984. Observations of aerosol chemical composition and acidity in northwest and southeast regions of the United States. *Science of the Total Environment* 39:125-133.

Anderson, D.E. 1978. Monitoring acid precipitation with an automatic precipitation collector and pH analyzer. M.S. thesis, University of Maryland, College Park, MD.

Anderson, B.J., and V.W. Keller. 1983. Acidic deposition production mechanism. Pp. 155-159 in A. Potter (ed), *Space Shuttle Environmental Effects: The First Five Flights.* National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, TX.

Anspaugh, L.R. 1987. Retention by vegetation of radionuclides derosited in rainfall—a literature summary. Lawrence Livermore National Laboratory, Livermore, CA.

Applin, K.R., and J.J. Jersak. 1986. Effects of airborne particulate matter on the acidity of precipitation in central Missouri. *Atmospheric Environment* 20:965-969.

Beauford, W., J. Barber, and A.R. Barringer. 1977. Release of particles containing metals from vegetation into the atmosphere. *Science* 195:571-573.

Benner, W.H., P.M. McKinney, and T. Novakov. 1985. Oxidation of SO_2 in fog droplets by primary oxidants. *Atmospheric Environment* 19:1377-1383.

Biddulph, O., R. Cory, and S. Biddulph. 1956. The absorption and translocation of sulfur in red kidney bean. *Plant Physiology* 31:28.

Blanpied, G.D. 1979. Effect of artificial rain water pH and calcium concentration on the calcium and potassium in apple leaves. *HortScience* 14:706-708.

Brewer, R.L., R.J. Gordon, L.S. Shepard, and E.C. Ellis. 1983. Chemistry of mist and fog from the Los Angeles area. *Atmospheric Environment* 17:2267-2270.

Brimblecombe, P. 1978. "Dew" as a sink for sulphur dioxide. *Tellus* 30:151-157.

Brimblecombe, P., and I.J. Todd. 1977. Sodium and potassium in dew. *Atmospheric Environment* 11:649-650.

Bytnerowicz, A., P.J. Temple, and O.C. Taylor. 1986. Effects of simulated acid fog on leaf acidification and injury development of pinto beans. *Canadian Journal of Botany* 64:918-922.

Cadle, S.H., and P.J. Groblicki. 1983. The composition of dew in an urban area. Pp. 17-29 in P.J. Samson (ed), *The Meteorology of Acid Deposition.* Air Pollution Control Association, Pittsburgh, Pennsylvania.

Cerling, T.E., and A.J. Alexander. 1987. Chemical composition of hoarfrost, rime and snow during a winter inversion in Utah, U.S.A. *Water, Air, and Soil Pollution* 35:373-379.

Chamberlain, A.C. 1975. The movement of particles in plant communities. Pp. 155-203 in J.L. Monteith (ed), *Vegetation and the Atmosphere, Vol. 1.* Academic Press, London.

Chameides, W.L. 1987. Acid dew and the role of chemistry in the dry deposition of reactive gases to wetted surfaces. *Journal of Geophysical Research* 92:11895-11908.

Chan, W.H., A.J.S. Tang, D.H.S. Chung, and N.W. Reid. 1987. An analysis of precipitation chemistry measurements in Ontario. *Environmental Science and Technology* 21:1219-1224.

Chapman, E.G., D.S. Sklarew, and J.S. Flickinger. 1986. Organic acids in springtime Wisconsin precipitation samples. *Atmospheric Environment* 20:1717-1725.

Cofer, W.R., III, G.L. Pellett, D.I. Sebacher, and N.T. Wakelyn. 1983. Aluminum oxychloride formation on space shuttle exhaust alumina. Pp. 141-147 in A. Potter (editor), *Space Shuttle Environmental Effects: The First Five Flights*. National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, TX.

Coulombe, H.N., and C.F. Cooper, editors. 1975. Ecolgoical Assessment of Vandenberg Air Force Base, California, Vol. I: Evaluation and Recommendations. Air Force Office of Scientific Research, Bolling AFB, DC.

Craker, L.E., and D. Bernstein. 1984. Buffering of acid rain by leaf tissue of selected crops. *Environmental Pollution*. 36:375-381.

Cronan, C.S., and W.A. Reiners. 1980. Canopy processing of acidic precipitation by coniferous and hardwood forests of New England. *Oecologia* 59:216-223.

Dasch, J.H. 1985. Measurement of dry deposition to a deciduous canopy. GMR-5019, ENV #203, General Motors Research Laboratories, Warren, MI.

Dolske, D.A., and D.F. Gatz. 1985. A field intercomparison of methods for the measurement of particle and gas dry deposition. *Journal of Geophysical Research* 90:2076-2084.

Dzubay, T.G., and R.K. Stevens. 1984. Composition and origins of aerosol at a forested mountain in Soviet Georgia. *Environmental Science and Technology* 18:873-882.

Eisenreich, S.J., B.B. Looney, and J.D. Thornton. 1981. Airborne organic contaminants in the Great Lakes ecosystem. *Environmental Science and Technology* 15:30-38.

Endress, A.G., T. J. Swiecki, and O.C. Taylor. 1978. Foliar and microscopic observations of bean leaves exposed to hydrogen chloride gas. *Environmental and Experimental Botany* 18:139-149.

Evans, L.S. 1982. Biological effects of acidity in precipitation on vegetation: a review. *Environmental and Experimental Botany* 22:155-169.

Evans, L.S., and T.M. Curry. 1979. Differential responses of plant foliage to simulated acid rain. *American Journal of Botany* 66:953-962.

Evans, L.S., N.F. Gmur, and F. da Costa. 1977. Leaf surface and histological perturbations of leaves of *Phaseolus vulgaris* and *Helianthus annuus* after exposure to simulated acid rain. *American Journal of Botany* 64:903-913.

Evans, L.S., K. A. Santucci, and M.J. Patti. 1985. Interactions of simulated rain solutions and leaves of *Phaseolus vulgaris* L. *Environmental and Experimental Botany* 25:31-40.

Fairfax, J.A.W., and N.W. Lepp. 1975. Effect of simulated 'acid rain' on cation loss from leaves. *Nature* 255:324-325.

Ferek, R.J., A.L. Lazrus, P.L. Haagenson, and J.W. Winchester. 1983. Strong and weak acidity of aerosols collected over the northeastern United States. *Environmental Science and Technology* 17:316-324.

Fortmann, R.C., and D.L. Johnson. 1984. Characterisation of individual ambient aerosol particles retained on *Taxus* needles washed with water. *Environmental Pollution* 8:1-6.

Fowler, D. 1980. Removal of sulphur and nitrogen compounds from the atmosphere in rain and by dry deposition. Pp. 22-32 in D. Drablos and A. Tollan (eds), *Ecological Impact of Acid Precipitation*. SNSF Project, Oslo, Norway.

Frevert, T., and O. Klemm. 1984. Wie andern sich pH-Werte im Regen- und Nebelwasser beim Abtrocknen auf Pflanzenoberflachen? *Archives for Meterology, Geophysics, and Bioclimatology* B34:75-81.

Fuzzi, S., G. Orsi, and M. Mariotti. 1983. Radiation fog liquid water acidity at a field station in the Po Valley. *Journal of Aerosol Science* 14:135-138.

Fuzzi, S., R.A. Castillo, J.E. Jiusto, and G.G. Lala. 1984. Chemical composition of radiation fog water at Albany, New York, and its relationship to fog microphysics. *Journal of Geophysical Research* 89:7159-7164.

Gaffney, J.S., G.E. Streit, W.D. Spall, and J.H. Hall. 1987. Beyond acid rain. *Environmental Science and Technology* 21:519-524.

Galloway, J.N., Z. Dianwu, X. Jiling, and G.E. Likens. 1987. Acid rain: China, United States, and a remote area. *Science* 236:1559-1562.

Garland, J.A. 1978. Dry and wet removal of sulphur from the atmosphere. *Atmospheric Environment* 12:349-362.

Garsed, S.G., and A. Mochrie. 1980. Translocation of sulphite in *Vicia faba* L. *New Phytologist* 84:421-428.

Glotfelty, D.E., J.N. Seiber, and L.A. Liljedahl. 1987. Pesticides in fog. *Nature* 325:602-605.

Granett, A.L., and R.G. Musselman. 1984. Simulated acidic fog injures lettuce. *Atmospheric Environment* 18:887-890.

Granett, A.L., and O.C. Taylor. 1981a. Diurnal and seasonal changes in sensitivity of plants to short exposures of hydrogen chloride gas. *Agriculture and Environment* 6:33-42.

Granett, A.L., and O.C. Taylor 1981b. The effect of designated pollutants on plant species, Fifth Annual Report. Air Force Aerospace Medical Research Laboratory, Wright-Patterson AFB, OH.

Haines, B., M. Stefani, and F. Hendrix. 1980. Acid rain: threshold of leaf damage in eight plant species from a southern Appalachian forest succession. *Water, Air, and Soil Pollution* 14:403-407.

Haines, B., J. Chapman, and C.D. Monk. 1985a. Rates of mineral element leaching from leaves of nine plant species from a southern Appalachian forest succession subjected to simulated acid rain. *Bulletin of the Torrey Botanical Club* 112:258-264.

Haines, B.L., J.A. Jernstedt, and H.S. Neufeld. 1985b. Direct foliar effects of simulated acid rain. II. Leaf surface characteristics. *New Phytologist* 99:407-416.

Heck, W.W., L.S. Bird, M.E. Bloodworth, W.J. Clark, D.R. Darling, and M.B. Porter. 1962. Environmental pollution by missile propellants. MRL-TDR-62-38, Aerospace Medical Division, Wright-Patterson AFB, OH.

Hidy, G.M. et al. 1975. Summary of the California aerosol characterization experiment. *Journal of the Air Pollution Control Association* 25:1106-1114.

Hileman, B. 1983. Acid fog: new findings widen the range of acid deposition phenomena. *Environmental Science and Technology* 17:117A-120A.

Hindawi, I.J., J.A. rea, and W.L. Griffis. 1980. Response of bush bean exposed to acid mist. *American Journal of Botany* 67:168-172.

Hocking, D., and M.B. Hocking. 1977. Equilibrium solubility of trace atmospheric sulfur dioxide in water and its bearing on air pollution injury to plants. *Environmental Pollution* 9:57-64.

Houghton, H.G. 1955. On the chemical composition of fog and cloud water. *Journal of Meterology* 12:355-357.

Hull, C.H., and N.H. Nie, editors. 1981. *SPSS Update 7-9.* McGraw Hill Book Co., New York.

Hutchinson, T.C., and C.M. Adams. 1987. Comparative abilities of leaf surfaces to neutralize acidic raindrops. I. The influence of calcium nutrition and charcoal-filtered air. *New Phytologist* 106:169-183.

Hutchinson, T.C., C.M. Adams, and B.A. Gaher. 1986. Neutralization of acidic raindrops on leaves of agricultural crop and boreal forest species. *Water, Air, and Soil Pollution* 31:475-484.

Ingestad, T. 1971. A definition of optimum nutrient requirements in birch seedlings. II. *Physiologia Plantarum* 24:118-125.

Ingestad, T. 1982a. Mineral nutrition of wheat, rye, barley, and oat seedlings in nutrient solutions. *Swedish Journal of Agricultural Research* 12:185-192.

Ingestad, T. 1982b. Relative addition rate and external concentration: driving variables used in plant nutrition research. *Plant, Cell and Environment* 5:443-453.

Ingestad, T. 1987. New concepts on soil fertility and plant nutrition as illustrated by research on forest trees and stands. *Geoderma* 40:237-252.

Ingestad, T., and V. Stoy. 1982. Mineral nutrition of wheat, rye, barley, and oat seedlings in nutrient solution. *Swedish Journal of Agricultral Research* 12:185-192.

Jacob, D.J., J.M. Waldman, J.W. Munger, and M.R. Hoffmann. 1984. A field investigation of physical and chemical mechanisms affecting pollutant concentrations in fog droplets. *Tellus* 36B:272-285.

Jacob, D.J., J.M. Waldman, J.W. Munger, and M.R. Hoffman. 1985. Chemical composition of fogwater collected along the California coast. *Environmental Science and Technology* 19:730-736.

Jacob, D.J., J.W. Munger, J.M. Waldman, and M.R. Hoffmann. 1986. The H_2SO_3-HNO_3-NH_3 system at high humidities and in fogs. 1. Spatial and temporal patterns in the San Joaquin Valley of California. *Journal of Geophysical Research* 91:1073-1088.

Jacobson, J.S. 1984. Effects of acidic aerosol, fog, mist and rain on crops and trees. *Philosophical Transactions of the Royal Society of London.* B305:327-338.

Jacobson, J.S., J. Osmeloski, K. Yamada, and L. Heller. 1987. The influence of simulated acidic rain on vegetative and reproductive tissues of cucumber (*Cucumis sativus* L.). *New Phytologist* 105:139-147.

Jyung, W.H., and S.H. Wittwer. 1964. Foliar absorption - an active uptake process. *American Journal of Botany* 51:437-444.

Kawamura, K., and I.R. Kaplan. 1986. Biogenic and anthropogenic organic compouonds in rain and snow samples collected in southern California. *Atmospheric Environment* 20:115-124.

Kelly, J.M., and R.C. Strickland. 1986. Throughfall and plant nutrient concentration response to simulated acid rain treatment. *Water, Air, and Soil Pollution* 29:219-231.

Khemani, L.T., G.A. Momin, P.S. Prakasa Rao, P.D. Safai, and P. Prakash. 1987. Influence of alkaline particulates on the chemistry of fog water at Delhi, north India. *Water, Air, and Soil Pollution* 34:183-189.

Knapp, W.W., V.C. Bowersox, B.I. Chevone, S.V. Krupa, J.A. Lynch, and W.W. McFee. 1988. Precipitation chemistry in the United States, Part 1: Summary of Ion Concentration Variability, 1979-1984. U.S. Department of Agriculture, Cooperative State Research Service, Washington, DC.

Knott, W., III, A. Koller, Jr., and J. Puleo. 1983. Environmental effects of STS-1 through STS-4 launches: comprehensive report. Pp. 1-30 in A. Potter (ed), Space Shuttle Environmental Effects: The First Five Flights. National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, TX.

Lee, Y.-N., and S.E. Schwartz. 1981. Evaluation of the rate of uptake of nitrogen dioxide by atmospheric and surface liquid water. *Journal of Geophysical Research* 86:11971-11983.

Lendzian, K.J. 1984. Permeability of plant cuticles to gaseous air pollutants. Pp. 77-81 in M.J. Koziol and F.R. Whatley (editors), Gaseous Air Pollutants and Plant Metabolism. Butterworth Scientific, London.

Lerman, S. 1976. Environmental quality research: the phytotoxicity of missile exhaust products - short term exposures of plants to HCl, H, and Al_2O_3. AMRL-TR-75-102, Wright-Patterson AFB, OH.

Lindberg, S.E., and G.M. Lovett. 1985. Field measurements of particle dry deposition rates to foliage and inert surfaces in a forest canopy. *Environmental Science and Technology* 19:236-244.

Lindberg, S.E., G.M. Lovett, D.D. Richter, and D.W. Johnson. 1986. Atmospheric deposition and canopy interactions of major ions in a forest. *Science* 231:141-145.

Lovett, G.M., and S.E. Lindberg. 1985. Application of surrogate surface and leaf extraction methods to estimation of dry deposition to plant canopies. Pp. 837-848 in H.R. Pruppacher, R.G. Semonin, and W.G.I. Slinn (editors), Precipitation Scavenging, Dry Deposition, and Resuspension. Elsevier Science Publishing, New York.

Lovett, G.M., S.E. Lindberg, D.D. Richter, and D.W. Johnson. 1985. The effects of acidic deposition on cation leaching from three deciduous forest canopies. *Canadian Journal of Forest Research* 15:1055-1060.

Madsen, B.C. 1981. Acid rain at Kennedy Space Center, Florida: recent observations. *Atmospheric Environment* 15:853-862.

McFarlane, J.C., and W.L. Berry. 1974. Cation penetration through isolated leaf cuticles. *Plant Physiology* 53:723-727.

McLaughlin, S.B. 1985. Effects of air pollution on forests: a critical review. *Journal of the Air Pollution Control Association* 35:512-534.

Mecklenburg, R.A., H.B. Tukey, Jr., and J.V. Morgan. 1966. A mechanism for the leaching of calcium from foliage. *Plant Physiology* 41:610-613.

Miller, H.G., and J.D. Miller. 1980. Collection and retention of atmospheric polllutants by vegetation. Pp. 33-40 in D. Drablos and A. Tollan (editors), Ecological Impact of Acid Precipitation. SNSF Project, Oslo, Norway.

Miller, D.R., J.E. Byrd, and M.J. Perona. 1987. The source of Pb, Cu, and Zn in fogwater. *Water, Air, and Soil Pollution* 32:329-340.

Moller, D., and R. Zierath. 1986. On the composition of precipitation water and its acidity. *Tellus* 38B:44-50.

Monteith, J.L. 1957. Dew. *Quarterly Journal of the Royal Meteorological Society* 83:322-341.

Mrose, H. 1966. Measurements of pH, and chemical analysis of rain, snow, and fog-water. *Tellus* 18:266-270.

Muir, P.S., T.V. Armentano, R.A. Pribush, and B.H. Carter. 1986a. Emissions scavenging by fog, dew, and foliage: foliage uptake and consequences for plants, Annual Technical Report for U.S. Air Force Office of Scientific Research. Holcomb Research Institute, Indianapolis, IN.

Muir, P.S., K.A. Wade, B.H. Carter, T.V. Armentano, and R.A. Pribush. 1986b. Fog chemistry at an urban midwestern site. *Journal of the Air Pollution Control Association* 36:1359-1361.

Muir, P.S., T.V. Armentano, R.A. Pribush, and B.H. Carter. 1987. Emissions scavenging by fog, dew, and foliage: foliage uptake and consequences for plants, Annual Technical Report for U.S. Air Force Office of Scientific Research. Holcomb Research Institute, Indianapolis, IN.

Mulawa, P.A., S.H. Cadle, F. Lipari, C.C. Ang, and R.T. Vandervennet. 1986. Urban dew: its composition and influence on dry deposition rates. *Atmospheric Environment* 20:1389-1396.

Munger, J.W., and S.J. Eisenreich. 1983. Continental-scale variations in precipitation chemistry. *Environmental Science and Technology* 17:32A-42A.

Munger, J.W., D.J. Jacob, J.M. Waldman, and M.R. Hoffman. 1983. Fogwater chemistry in an urban atmosphere. *Journal of Geophysical Research* 88:5109-5121.

Musselman, R.C. 1988. Acid neutralizing capacity of leaves exposed to acidic fog. *Environmental and Experimental Botany* 28:27-32.

Musselman, R.C., and J.L. Sterrett. 1988. Sensitivity of plants to acid fog. *Journal of Environmental Quality* 17:329-333.

National Acid Deposition Program. 1984. NADP quality assurance plan - deposition monitoring. Natural Resource Ecology Laboratory, Fort Collins, CO.

National Acid Deposition Program. 1987. Annual data summary: precipitation chemistry in the United States - 1986. Natural Resource Ecology Laboratory, Fort Collins, CO.

National Aeronautics and Space Administration. 1978. Final Environmental Impact Statement: Space Shuttle Program. Washington, DC.

Neufeld, H.S., J.A. Jernstedt, and B.L. Haines. 1985. Direct foliar effects of simulated acid rain. II. Damage, growth and gas exchange. *New Phytologist* 99:389-405.

Olson, R.K., W.A. Reiners, and G.M. Lovett. 1985. Trajectory analysis of forest canopy effects on chemical flux in throughfall. *Biogeochemistry* 1:361-373.

Pellett, G.L., D.I. Sebacher, R.J. Bendura, and D.E. Wornom. 1983. HCl in rocket exhaust clouds: atmospheric dispersion, acid aerosol characteristics, and acid rain deposition. *Journal of the Air Pollution Control Association* 33:304-311.

Percy, K.E., and E.A. Baker. 1987. Effects of simulated acid rain on production, morphology and composition of epicuticular wax and on cuticular membrane development. *New Phytologist* 107:577-589.

Pierson, W.R., W.W. Brachaczek, R.A. Gorse, Jr., S.M. Japar, and J.M. Norbeck. 1986. On the acidity of dew. *Journal of Geophysical Research* 91:4083-4096.

Potter, A.E. 1978. Environmental effects of the Space Shuttle. *Journal of Environmental Science* 21:15-21.

Pyilpec, B., and R.E. Redmann. 1984. Acid-buffering capacity of foliage from boreal forest species. *Canadian Journal of Botany* 62:2650-2653.

Reiners, W.A., and R.K. Olson. 1984. Effects of canopy components on throughfall chemistry: an experimental analysis. *Oecologia* 63:320-330.

Reiners, W.A., R.K. Olson, L. Howard, and D.A. Schaefer. 1986. Ion migration from interiors to outer surfaces of balsam fir needles during dry, interstorm periods. *Environmental and Experimental Botany* 26:227-231.

Salisbury, F.B., and C.W. Ross. 1978. Plant Physiology, 2nd edition. Wadsworth Publishing Co., Belmont, CA.

Scherbatskoy T., and R.M. Klein. 1983. Response of spruce and birch foliage to leaching by acidic mists. *Journal of Environmental Quality* 12:189-195.

Schindler, D.W. 1988. Effects of acid rain on freshwater ecosystems. *Science* 239:149-157.

Schutt, P., and E.B. Cowling. 1985. Waldsterben, a general decline of forests in central Europe: symptoms, development and possible causes. *Plant Disease* 69:548-558.

Sebacher, D.I., W.R. Cofer, III, D.C. Woods, and G.L. Maddrea, Jr. 1984. Hydrogen chloride and aerosol ground cloud characteristics resulting from space shuttle launches. *Atmospheric Environment* 18:763-770.

Sokal, R.R., and F.J. Rohlf. 1981. Biometry, 2nd edition. W.H. Freeman and Co., San Francisco, CA.

Stevens, R.K., T.G. Dzubay, R.W. Shaw, W.A. McClenny, C.W. Lewis, and W.E. Wilson. 1980. Characterization of the aerosol in the Great Smoky Mountains. *Environmental Science and Technology* 4:1491-1498.

Swoboda, G.D. 1983. STS-5 exhaust product ground deposition. Pp. 39-45 in A. Potter (editor), Space Shuttle Environmental Effects: The First Five Flights. National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, TX.

Takemoto, B.K., D.M. Olszyk, A.G. Johnson, and C.R. Parada. 1988. Yield responses of field-grown crops to acidic fog and ambient ozone. *Journal of Environmental Quality* 17:192-197.

Thorne, P.G., G.M. Lovett, and W.A. Reiners. 1982. Experimental determination of droplet impaction on canopy components of balsam fir. *Journal of Applied Meteorology* 21:1413-1416.

Trites, L.F., and R.G.S. Bidwell. 1985. Effect of acidic precipitation on bean plants. *Canadian Journal of Botany* 65:1121-1126.

Tukey, H.B., Jr. 1970. The leaching of substances from plants. *Annual Review of Plant Physiology* 21:305-324.

Tukey, H.B., Jr., H.B. Tukey, and S.H. Wittwer. 1958. Loss of nutrients by foliar leaching as determined by radioisotopes. *Proceedings of the American Society of Horticultural Science* 71:496-505.

Unsworth, M.H. 1984. Evaporation from forests in cloud enhances effects of acid deposition. *Nature* 312:262-264.

Voldner, E.C., L.A. Barrie, and A. Sirois. 1986. A literature review of dry deposition of oxides of sulphur and nitrogen with emphasis on long-range transport modelling in North America. *Atmospheric Environment* 20:2101-2123.

Waldman, J.M., and M.R. Hoffman. 1988. Nutrient leaching from pine needles impacted by acidic cloudwater. *Water, Air, and Soil Pollution* 37:193-201.

Waldman, J.M., J. W. Munger, D.J. Jacob, R.C. Flagan, J.J. Morgan, and M.R. Hoffman. 1982. Chemical composition of acid fog. *Science* 218:677-680.

Whitby, K.T. 1978. The physical characteristics of sulfur aerosols. *Atmospheric Environment* 12:135-159.

Wilkinson, L. 1984. SYSTAT: The System for Statistics. SYSTAT, Inc., Evanston, IL.

Wisniewski, J. 1982. The potential acidity associated with dews, frosts, and fogs. *Water, Air, and Soil Pollution* 17:361-377.

Wood, T., and F.H. Bormann. 1975. Increases in foliar leaching caused by acidification of an artificial mist. *Ambio* 4:169-171.

Yaalon, D.H., and E. Ganor. 1968. Chemical composition of dew and dry fallout in Jerusalem, Israel. *Nature* 217:1139-1140.

Yamada, Y., S.H. Wittwer, and M.J. Bukovac. 1964. Penetration of ions through isolated cuticles. *Plant Physiology* 39:28-32.

Zammit, C.A., and P.H. Zedler. 1988. Germination response to extreme acidity: impact of simulated acid deposition from a single shuttle launch. *Environmental and Experimental Botany* 28:73-81.

APPENDIX

1986 PUBLICATION ON ACID FOGS IN INDIANAPOLIS

Fog Chemistry at an Urban Midwestern Site

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Strongly acidic fogs and clouds have been documented from several sites in the United States and Europe, including southern California,[1-5] mountaintops in the northeastern United States,[6] the Po Valley in Italy,[7] and, most recently, a suite of sites in the eastern United States ranging from Maine to Virginia.[8] The potential for these acidic events to damage materials, crops, native vegetation, and public health has been discussed,[1-9] and research efforts are underway to assess the magnitude of these effects.

While researchers are beginning to understand the chemistry of clouds and fogs from these areas and how it compares to rain chemistry, to our knowledge no studies of the chemistry of fogs from the midwestern United States have been published to date. Emissions of potentially acidifying sulfur and nitrogen compounds from some midwestern states are among the highest in the nation.[10,11] Hence, the potential clearly exists for fog in these regions to scavenge such pollutants and to become highly acidic.

In Indianapolis, dense fogs (visibility ≤ 0.4 km) occur an average of 20 days per year (21-yr mean for interval 1964–1984 = 19.5 days, data from National Weather Service for Indianapolis International Airport), a moderate fog frequency when contrasted with coastal and moist Appalachian sites.[12] Light fogs (visibility > 0.4 km) occur more frequently than dense fogs, particularly during summer when they are often associated with regional haze, relatively stagnant air, and elevated levels of sulfate aerosols which may result in highly acidic fog water.

The Holcomb Research Institute is monitoring fog chemistry in Indianapolis, Indiana and at sites in and near the heavily industrialized Ohio River Valley. Results reported here indicate that fogs in this area can be strongly acidic, and that further studies are warranted. We report 1) the ionic composition of three fog events, samples collected in Indianapolis between December 1985 and February 1986, and 2) the pH of three additional events, samples collected between November 1985 and February 1986. (The volume of fog collected during the latter three events was insufficient for chemical analysis other than pH.) The pH of the fog samples ranged from 2.85 to 4.06: some of this fell within the range known to damage foliage and yield of some plant species.[9,13] It has been demonstrated that even one exposure to highly acidic mists (pH ≤ 2.5) can damage certain crop species[14]; hence, it is important to document the occurrence of any events having acidity near this level.

Study Area and Methods

All fog samples were collected from the Butler University Environmental Preserve, an 8-ha study area on the flood plain of the White River in Indianapolis, and located approximately 8 km northwest of the center of the city. Most major industrial and utility sources of air pollutants are south of the study area. Six of the fog events were sampled with a Cal Tech rotating arm collector (RAC)[15]; one of the six events was also sampled with a Cal Tech active strand collector that gathers droplets on slanted Teflon screens.[16] Our active strand collector is a slightly modified version of the Cal Tech active strand collector; the strand diameter in our instrument is 510 μm, its sampling flow is 24.5 m³/min, it samples 86 percent of the air passing through it, and its theoretical 50 percent cut size is 3.8 μm.[17] The samplers were located on open, level ground in an old-field portion of the preserve. The ground was frozen during all collections, and was intermittently snow-covered.

Fog samples (in clean polypropylene bottles) were returned immediately to the Holcomb Research Institute/But-

ler University analytical laboratory where the pH of a small aliquot was determined promptly (using a semimicro combination electrode, and calibration with National Bureau of Standards buffer solutions). Samples were then treated with chloroform (0.2 mL/ 100 mL) and stored in darkness at 4°C in tightly closed bottles until they were analyzed. Anions and ammonium were determined by ion chromatography (Dionex Model 2010i). Major cations were determined on a Perkin-Elmer 305B atomic absorption spectrophotometer using an air-acetylene flame. A releasing agent (lanthanum) was added to the sample for Ca and Mg analysis.

Results

The chemistry of fog samples is given in Table I. All ion balances were within ±10 percent. (Ion balances were calculated on an equivalent basis as a percent difference between anion and cation species present at a given pH.) Conditions under which samples were collected are given in Table II. All sampled were acidic, and the range of acidities encompassed more than an order of magnitude. The lowest pH measured was 2.85: all events but one (that sampled with both collectors, hence appearing twice in Table I) had pH < 4.0, and four events had pH ≤ 3.33. No correlation is apparent between either visibility or direction of the prevailing wind and acidity of the fogs (Tables I and II).

Sulfate and nitrate were the dominant anions in all samples, while hydrogen and ammonium dominated the cations in most samples (Table I), as has been found for fogs in other environments.[3,8] Sulfate concentrations varied widely both within and between fog events (Table I), but were generally lower than those recently reported for a summer acidic cloud/fog event in the

eastern United States.[8] However, sulfate concentrations were generally higher than those reported for autumn radiation fogs at Albany, New York[18] and for late autumn or winter fogs in Los Angeles.[2] Sulfate concentrations of fog water collected elsewhere in California vary widely depending on site and date, with some concentrations lower and some higher than those reported here.[1,3,4]

Concentrations of nitrate in the fog waters varied widely between events (Table I), covering a range similar to that recently reported for a widespread acidic cloud-fog event in the eastern United States.[3] Nitrate concentrations in the Indianapolis fogs were higher than those found for autumn fog water at Albany, New York[18] and were generally lower than those for urban area fog samples in California.[1,2,3]

Ratios of sulfate to nitrate in the fog samples varied widely both between and within events (Table I). More data are required before any generalizations can be made concerning the relative contributions of these ions to fog water chemistry in Indianapolis.

The rotating arm and active strand collectors operated over nearly the same time interval during one event (0800–0910 h and 0800–0915 h respectively, Table I), allowing us to make a limited comparison of chemical concentrations in fogwater collected by the two instruments, and of their fogwater collection rates. The ratios of ions collected by the strand collector to those collected by the rotating arm collector were comparable to previously published ratios,[16] ranging from 1.44 (for K^{+}) to 0.80 (for Ca^{2+}) with an overall average of 1.15. The strand collector had a fog water collection rate 2.65 times that of the rotating arm collector, similar to a previously published comparison;[16] however, we are puzzled by the discrepancy in the liquid water content estimates derived from the two

Table II. Conditions during fog sampling.

Date	Temperature, °C[a]	Surface wind velocity (m/sec) and direction[a]	Visibility, m[b]	Precipitation[b]	Estimated fog liquid water content, g/m[c]
11/25/85	4	4.5 E	400–600	light drizzle	.06
12/09/85	−3–0	2 NNW	60	no drizzle	.04
12/10/85	6	3 NNW	100–400	light drizzle	.05
01/23/86	−4–0	1 NW	30–180	no drizzle	.02
02/02/86	1	3 NNE	120–800	no drizzle	.01
0800–0910[d]	8	0–2 SSW	30–60	light drizzle	.14 (.06)
0915–1020	9	0–4 SW	30–90	no drizzle	— (.06)
1020–1030	10	4 SW	400–1200	no drizzle	— (—)

[a] Temperature and wind data from Indianapolis International Airport, 14 km SW of study area.
[b] Estimated at collecting site.
[c] Liquid water content of fogs was estimated using the volume of liquid collected, the duration of sampling, the rate at which the instruments sample air, and the average collection efficiency of the instruments. Estimates were based on samples collected by the rotating arm collector, which samples air at a rate of 5 m[3]/min and has an average collection efficiency of 60%.[15] Estimates in parentheses for 2/18/86 were based on samples collected by the active strand collector, which samples air at a rate of 21.1 m[3]/min and has an average collection efficiency of 85%.[17]
[d] Time intervals during which samples were collected using the active strand collector.

Table I. Ionic composition of fogs collected in Indianapolis, Indiana. Samples for which only data on hydrogen ion are given had insufficient volume for further chemical analysis.

Date and collector[a]	Volume collected (mL)[b]	pH	SO₄⁼	NO₃⁻	Cl⁻	PO₄³⁻	H⁺	NH₄⁺	Ca²⁺	Mg²⁺	K⁺	Na⁺
12/9/85 0945–1150 RAC	16	3.10	731	943	68.3	165	794	676	100	37	11	26
1/23/86 0915–1223 RAC	10	3.76	1240	1000	140	727	174	1300	808	226	19	108
2/18/86 0800–0910 RAC	30	4.03	604	236	114	180	93.3	671	25	8.1	4.1	17
2/18/86 0945–1020 RAC	11	3.92	391	353	114	121	120	743	35	14	7.2	30
2/18/86 0800–0915 strand	85	4.06	672	284	143	217	87.1	820	35	7.0	4.3	27
2/18/86 0915–1020 strand	75	3.78	589	344	185	222	166	787	31	3.2	4.9	32
2/18/86 1020–1030 strand	—	3.74	454	371	142	160	187	721	35	8.2	5.1	33
11/25/85 1630–1730 RAC	10	3.33					468					
12/10/85 1655–1745 RAC	8	3.17					676					
2/2/86 0840–1100 RAC	3	2.85					1410					

[a] Time is local time; "RAC" = rotating arm collector; "strand" = active strand collector.
[b] Volumes are approximate (± 0.1–0.5 mL).

samples (Table II). Possibly the light drizzle that occurred during sampling differentially influenced the collecting efficiency of the instruments, and such an effect would invalidate our calculations of liquid water content.

Rain and snow were collected weekly at the same Indianapolis site from which fog samples were collected, using a standard Aerochem Metrics wet-dry collector and following collection and analysis procedures of the National Atmospheric Deposition Program.[19,20] When compared to fog chemistries (Table I), rain/snow samples for the weeks when fog samples were collected had far lower concentrations of sulfate and nitrate, and were generally less acidic (Table III). The rain/snow samples were a composite from several events over a week and hence were not collected simultaneously with the fog collected during short intervals within each week. Nevertheless, the contrast between the ionic concentrations in rain/snow and the concentrations in fog is striking: such contrasts have been noted by others.[1,2]

ary 1986 averaged 71.9 μEq/L (standard error = 9.72 μEq/L). More data on fog frequency, duration, and rates of deposition to surfaces are required to evaluate whether fog water in urban midwestern sites may be an injurious agent.

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Table III. Concentration of hydrogen, sulfate, and nitrate ions (μEq/L) in rain water collected weekly in Indianapolis, IN. Weeks for which data are given include dates when fogs were collected.

Date	Ionic composition (μEq/L)			
	pH	H$^+$	SO$_4^=$	NO$_3^-$
Nov. 19–26, 1985	4.01	97.7	48.9	19.8
Dec. 3–10, 1985	4.17	67.6	54.5	31.2
Jan. 21–28, 1986	4.07	85.1	70.4	101.1
Jan. 28–Feb. 4, 1986	4.26	54.9	51.6	24.7
Feb. 11–18, 1986	3.94	114.8	105.7	82.4

Conclusions

Fog water samples collected in late fall and winter in Indianapolis were acidic; however, fog chemistry data throughout the year are needed to assess more fully the potential for fog water to influence materials, vegetation, or public health either positively or negatively. For example, concentrations of sulfate in Indianapolis summer fogs are probably higher than those reported here because summer temperature, light, and humidity are more conducive to sulfate formation than are winter conditions,[10,21] and because pre-existing aerosols may be major determinants of fog water chemistry.[1] We cannot substantiate this hypothesis directly, as sulfate aerosols are not measured or modeled in Indianapolis, however data on sulfate in weekly rain samples collected at our Indianapolis study site suggest that summer sulfate loadings are higher than winter loadings. Sulfate in rain for July and August 1985 averaged 90.8 μEq/L (standard error = 7.07 μEq/L) while sulfate in rain and snow for January and Febru-

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References

1. J. M. Waldman, J. W. Munger, D. J. Jacob, R. C. Flagan, J. J. Morgan, M. R. Hoffmann. "Chemical composition of acid fog." *Science* 218: 677 (1982).
2. R. L. Brewer, R. J. Gordon, L. S. Shepard, E. C. Ellis. "Chemistry of mist and fog from the Los Angeles urban area." *Atmos. Environ.* 17: 2267 (1983).
3. J. W. Munger, D. J. Jacob, J. M. Waldman, M. R. Hoffmann, "Fogwater chemistry in an urban atmosphere." *J. Geophys. Res.* 88: 5109 (1983).
4. D. J. Jacob, J. M. Waldman, J. W. Munger, M. R. Hoffmann, "Chemical composition of fogwater collected along the California coast," *Environ. Sci. Technol.* 19: 730 (1985).
5. J. M. Waldman, J. W. Munger, D. J. Jacob, M. R. Hoffmann, "Chemical characterization of stratus cloudwater and its role as a vector for pollutant deposition in a Los Angeles pine forest." *Tellus* 37B: 91 (1985).
6. R. E. Falconer, P. D. Falconer, "Determination of cloud water acidity at a

mountain observatory in the Adirondack Mountains of New York State." *J. Geophys. Res.* 85: 7465 (1980).
7. S. Fuzzi, G. Orsi, M. Mariotti, "Radiation fog liquid water acidity at a field station in the Po Valley." *J. Aerosol Sci.* 14: 135 (1983).
8. K. C. Weathers, G. E. Likens, F. H. Bormann, J. S. Eaton, W. B. Bowden, J. L. Anderson, D. A. Cass, J. N. Galloway, W. S. Keene, K. D. Kimball, P. Huth, D. Smiley, "A regional acidic cloud/fog water event in the eastern United States," *Nature* 319: 657 (1986).
9. J. S. Jacobson, "Effects of acidic aerosol, fog, mist and rain on crops and trees," *Philosophical Trans. Roy. Soc. London* 305: 327 (1984).
10. "Acid Rain and Transported Air Pollutants: Implications for Public Policy," U.S. Congress, Office of Technology Assessment, OTA-0-204, Washington, DC, 1984.
11. G. Gschwandtner, K. Gschwandtner, K. Eldridge, C. Mann, D. Mobley, "Historic emissions of sulfur and nitrogen oxides in the United States from 1900 to 1980." *JAPCA* 36: 139 (1986).
12. J. Wisniewski, "The potential acidity associated with dews, frosts, and fogs." *Water, Air, Soil Pollut.* 17: 361 (1982).
13. L. S. Evans, "Botanical aspects of acidic precipitation." *Botan. Rev.* 50: 449 (1984).
14. A. L. Granett, R. C. Musselman, "Simulated acidic fog injures lettuce." *Atmos. Environ.* 18: 887 (1984).
15. D. J. Jacob, R. T. Wang, R. C. Flagan, "Fog water collector design and characterization." *Environ. Sci. Technol.* 18: 827 (1984).
16. D. J. Jacob, J. M. Waldman, M. Haghi, M. R. Hoffmann, R. C. Flagan, "An instrument to collect fog water for chemical analysis." *Rev. Sci. Instruments* 56: 1231 (1985).
17. B. Daube, Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology, Pasadena, California, private communication, 1986.
18. S. Fuzzi, R. A. Castillo, J. E. Jiusto, G. G. Lala, "Chemical composition of radiation fog water at Albany, New York, and its relationship to fog microphysics." *J. Geophys. Res.* 89: 7159 (1984).
19. "NADP Instruction Manual—Site Operation." National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 1982.
20. "NADP Quality Assurance Plan—Deposition Monitoring." National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO, 1984.
21. C. S. Sloane, "Summertime visibility declines: meteorological influences." *Atmos. Environ.* 17: 763 (1983).

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